with only slight differences in chemical shift and coupling constants ($\delta_A = 3.08$, $\delta_B = 2.75$; $J_{AB} = 12$, $^1/_2(J_{H_AP} + J_{H_BP}) = 0.3$ Hz in C_6D_6). A broad signal, at 11.55 ppm, was assigned to the ammonium proton. No changes in the spectra were observed down to −80 °C. The retention of the bicyclic structure is further ascertained by the close resemblance of the mass and infrared spectra of **9b** and **5b**.

By contrast, when the adduct of the noncyclic ligand **1c** was treated with HCl in comparable experimental conditions, it readily led (with 2 equiv of HCl) to the chlorophosphane adduct $CpMo(CO)_2[PCl(OEt)_2]Cl$ (**10c**) and dimethylammonium chloride, which were isolated in 70 and 90% yields, respectively, showing that the usual P–N bond cleavage reaction takes place in this case. Adduct **10c** was characterized by its elemental analysis and mass, infrared, ^{31}P NMR, and ^1H NMR spectra (Tables I and II).

These experiments establish that a phosphorus-bound nitrogen atom can display definite basicity when incorporated in constrained structures that require the nitrogen atom to adopt a pyramidal geometry.

Registry No. **1a**, 65693-26-7; **1b**, 75194-94-4; **1c**, 2632-87-3; *cis*-**5b**, 97466-39-2; *trans*-**5b**, 97466-40-5; *cis*-**6a**, 97416-61-0; *trans*-**6a**, 97466-41-6; *cis*-**6b**, 97416-62-1; *trans*-**6b**, 97466-42-7; *cis*-**6c**, 97416-63-2; *trans*-**6c**, 97466-43-8; *trans*-**7b**, 97416-64-3; *trans*-**8a**, 97416-65-4; *trans*-**8c**, 97416-66-5; (**9b**)(Cl^-), 97548-95-3; (**9b**)($CF_3SQ_3^-$), 97548-96-4; *cis*-**10c**, 97416-67-6; *trans*-**10c**, 97466-44-9; $(\eta^5\text{-}C_5H_5)Mo(CO)_3H$, 12176-06-6; $(\eta^5\text{-}C_5H_5)Mo(CO)_3Cl$, 12128-23-3; $(\eta^5\text{-}C_5H_5)Mo(CO)_3CH_3$, 12082-25-6.

Contribution from the Institut fur Anorganische Chemie, Technische Hochschule Darmstadt, D-6100 Darmstadt, West Germany, and Department of Chemistry, Western Washington University, Bellingham, Washington 98225

Metal Complexes of Tetrapyrrole Ligands. 36.[1] Proton NMR Spectra of Cobalt(II) 5,15-Dialkyl-5,15-dihydro-2,3,7,8,12,13,17,18-octaethylporphyrins (Decaalkylporphodimethenes)

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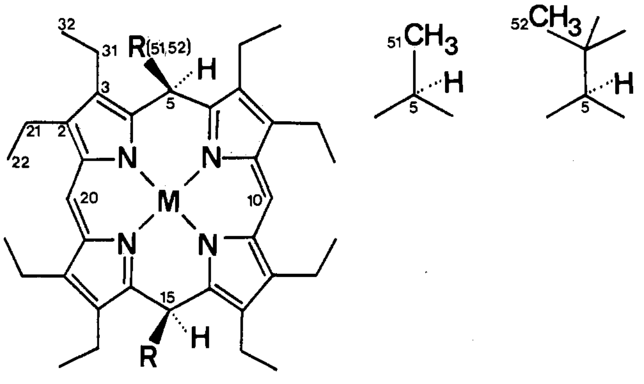
A series of four square-planar cobalt(II) 5,15-dialkyloctaethylporphodimethenes, $Co(OEPR_2)$, have been synthesized and their ^1H NMR spectra interpreted. All complexes were isolated as the stereoisomer in which the alkyl groups, R, are syn-axial. The complexes are low spin and have ^1H NMR spectra consistent with a $^2A\ (d_{z^2})^1$ ground state. The isotropic shifts are predominantly dipolar in origin and exhibit a linear $1/T$ dependence with non-zero intercept. The line widths (20–440 Hz) are determined exclusively by a dipolar relaxation mechanism with a short correlation time, $\tau_c = 2 \times 10^{-12}$ s. From an analysis of the relative isotropic shifts and relative line widths, the geometry of $Co(OEPR_2)$ in solution appears to be substantially nonplanar with both folding of the macrocycle and ruffling of the pyrrole rings. This is consistent with the known solid-state structures of metalloporphodimethenes.

During their work on the oxidation of uroporphyrinogens to uroporphyrins with iodine, Mauzerall and Granick[3] discussed the occurrence of porphomethenes (5,10,15,20-tetrahydroporphyrins) and porphodimethenes (5,15-dihydroporphyrins) as air-labile intermediates. Air-labile metal complexes of porphodimethenes were later found in photoreductions of zinc porphyrins[4] and chemical reductions of zinc or aluminum octaethylporphyrins.[5–7] In order to prepare these reduced tetrapyrrole complexes more readily, the reductive alkylation of metal complexes of octaethylporphyrin (OEP)[8] was developed.[1,6,8] This furnishes air-stable metal complexes of 5,15-dialkyl-5,15-dihydro-2,3,7,8,12,13,17,18-octaethylporphyrins (decaalkylporphodimethenes) of the general formula $M(OEPR_2)$ as shown in structures **1**–**4**.[9] While the direct reductive alkylation of zinc tetraphenylporphyrin, Zn(TPP),[10] does not produce the corresponding porphodimethene, a reductive addition of two allyl groups at 5,15-C of Fe(TPP) has been accomplished by Mansuy et al.[11]



1: $Co(OEPMe_2)$, $R = CH_3$
2: $Co(OEPEt_2)$, $R = C_2H_5$
3: $Co(OEPPr_2)$, $R = i\text{-}C_3H_7$
4: $Co(OEPBu_2)$, $R = t\text{-}C_4H_9$

According to the ^1H NMR data[7,10b] and several X-ray structure determinations by Scheidt et al.,[12] the alkyl groups introduced

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(8) Abbreviations used: $(OEP)^{2-}$, $(TPP)^{2-}$, $(TTP)^{2-}$, $(OEPR_2)^{2-}$, the dianions of octaethylporphyrin, *meso*-tetraphenylporphyrin, *meso*-tetra-*p*-tolylporphyrin, and 5,15-dialkyloctaethylporphodimethene, respectively; L, axial ligands; Im, imidazole; pip, piperidine.

(9) The numbering scheme applied in the formula fulfills the IUPAC numbering rules for the C atoms of the porphyrin skeleton. The second digit of the numbers 21, 22, 31, 32, 51, and 52 defines the first or second carbon in a side chain extending from the porphyrin positions 2, 3, 5, and the corresponding symmetry-related positions. 21,31-H are jointly referred to as α-CH_2 and 22,32-H as β-CH_3 protons.

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via reductive alkylation occupy the syn-axial 5,15-positions of the porphodimethene core, which is folded like a roof along the line connecting 5-C and 15-C. This has been found for the square-planar Ni(II) complex Ni(OEPMe$_2$)[12a] and all the other compounds investigated. For M(OEPMe$_2$)L the single axial ligand also takes the syn-axial (exo) position, as oxide or nitride in TiO(OEPMe$_2$)[12b] or MnN(OEPMe$_2$).[12c] When there are two ligands, as in the carbonylosmium(II) complex OsCO(OEPMe$_2$)py,[12d] the more firmly bound ligand resides in the syn-axial (exo) position.

For a series of porphodimethenes such as **1**–**4**, increasing steric hindrance is introduced to the axial coordination sites as the substituents R increase in size. Thus the 5,15-bis(*tert*-butyl)porphodimethene system does not allow syn-axial coordination of a fifth ligand.[12] The square-pyramidal hydroxoiron(III) and nitrosylcobalt(III) complexes Fe(OEPBu$_2$)OH[12e] and Co(OEPBu$_2$)NO[12f] both exist in the anti-axial configuration, the two *tert*-butyl groups residing on the "ridge of the roof" and the axial ligand below the roof.

Preliminary ^{1}H NMR work on the series of iron(III) porphodimethenes Fe(OEPMe$_2$)L and Fe(OEPBu$_2$)L (L = OMe, F, N$_3$, OCN, NCS, Cl, Br)[13] has shown that the isotropic shifts of the α-methylene protons varied significantly with the syn-axial substituents R and the axial ligands L. In order to understand this phenomenon, to see whether these spectra could serve to determine configurations in solution, and to study axial ligation processes, a systematic investigation of the ^{1}H NMR spectra of paramagnetic porphodimethene complexes has been undertaken. This paper will be primarily concerned with the ^{1}H NMR spectra of the cobalt(II) 5,15-dialkylporphodimethenes (**1**–**4**) and their relation to the cobalt(II) porphyrin spectra. Further publications will deal with the iron(III) and nickel(II) complexes and their NMR spectra.

The observed isotropic shift $(\Delta H/H)_{\text{iso}}$ for any proton is the sum of two components:[14]

$$(\Delta H/H)_{\text{iso}} = (\Delta H/H)_{\text{con}} + (\Delta H/H)_{\text{dip}} \qquad (1)$$

The contact shift $(\Delta H/H)_{\text{con}}$ is directly related to spin delocalization via covalency whereas the dipolar shift, $(\Delta H/H)_{\text{dip}}$, results from a dipolar, through-space, interaction and is related to the magnetic anisotropy and the geometry of the complex.

On this basis analysis of the NMR spectra of paramagnetic complexes, especially synthetic metalloporphyrins,[15,16] has afforded much information concerning the geometries of these species in solution, the mechanism of spin transfer and delocalization, and the effect of oxidation state and spin state upon spin transfer. Furthermore, these results have then been used as a basis for the analysis of the more complex spectra of naturally occurring hemes and heme proteins.[17]

The NMR spectra of paramagnetic metalloporphodimethenes share common features with those of the metalloporphyrins. However, because of the reduced symmetry and the 5,15-substituents, the porphodimethene spectra are decidedly more complex. For example, the planar octaethylporphyrin complex Co(OEP) has only three resonances in its NMR spectrum, whereas the related Co(OEPMe$_2$) (**1**) has nine resonances because of the folding of the porphodimethene and the resulting lower symmetry. This added complexity can have advantages. Although the NMR spectra of porphodimethenes may be more difficult to analyze, there is potentially more structural information to be extracted. Also because of the distinct asymmetry above and below the tetraaza plane in the porphodimethenes, one can infer from the NMR spectra whether axial ligation of a Lewis base occurs from the top or bottom side. In this regard, the 5,15-dialkylporphodimethenes are similar to picket fence porphyrins, which have been used to model oxygen binding of hemoglobin.[18]

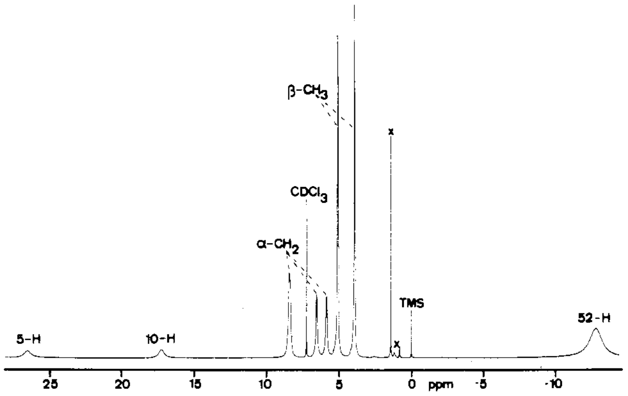

Figure 1. Proton NMR spectrum of Co(OEPBu$_2$) in CDCl$_3$ at 293 K (× denotes impurity).

Previous proton NMR studies of square-planar, low-spin cobalt(II) complexes have included the synthetic porphyrins[19–23] and Schiff base complexes.[24] Only the porphyrins and porphodimethenes have directly comparable spectra. Both have ^{2}A ground states with the electron configuration $(d_{z^2})^1$. Analysis of the cobalt(II) porphyrin NMR spectra[19,21,22] confirmed that the isotropic shifts were predominantly dipolar in origin. On this assumption, Co(TTP) has been used as a paramagnetic shift reagent and relaxation probe for determining the geometry of its adducts with various π donors and π acceptors.[20,21]

Experimental Section

Materials. The 5,15-dialkyl-5,15-dihydro-2,3,7,8,12,13,17,18-octaethylporphyrins H$_2$(OEPR$_2$) were synthesized as described previously.[1,10]

Alumina (Al$_2$O$_3$, I, neutral) was purchased from Woelm Pharmaceuticals and deactivated with water to grade III.

Synthesis of (5,15-Dialkyl-2,3,7,8,12,13,17,18-octaethylporphyrinato)cobalt(II) Complexes, Co(OEPR$_2$) (1–4). A mixture of 0.5 mmol of porphodimethene, H$_2$(OEPR$_2$), 480 mg (1.4 mmol) of Co$_2$(CO)$_8$, and 50 mg (0.2 mmol) of I$_2$ was refluxed under nitrogen in toluene for 1 h. The solution was taken to dryness in vacuo; the residue was chromatographed on Al$_2$O$_3$ (grade III) and eluted with cyclohexane/toluene (9:1) under nitrogen. The first, yellow-brown fraction yielded Co(OEPR$_2$) (**1**–**4**) as black rods after evaporation to dryness, recrystallization from cyclohexane, and drying at 45 °C (10^{-3} mm). Yields: **1**, 67%; **2**, 59%; **3**, 46%; **4**, 69%. Anal. **1** and **4** have been previously described.[13] Calcd for **2**, C$_{40}$H$_{54}$N$_4$Co (mol wt 649.8): C, 73.93; H, 8.37; N, 8.62. Found: C, 73.82; H, 8.37; N, 8.54. Calcd for **3**, C$_{42}$H$_{58}$N$_4$Co (mol wt 677.8): C, 74.41; H, 8.62; N, 8.26. Found: C, 74.51; H, 8.59; N, 8.10. IR (cm^{-1}, KBr; methene bands): **1**, 1611; **2**, 1619; **3**, 1605; **4**, 1615 cm^{-1}. UV/vis (toluene; broad bands with shoulders approximately 30 nm above and below the following $\lambda_{\max}$, nm (log ϵ): **1**, 461 (4.60); **2**, 462 (4.61); **3**, 457 (4.61); **4**, 461 (4.62). Mass spectra (*m/e*) showed the molecular ions (**1**, 621; **2**, 649; **3**, 677; **4**, 705) and the typical cracking pattern explained earlier,[10] i.e. successive losses of one or two of the 5,15-alkyl groups.

Magnetic Resonance. The ^{1}H NMR spectra were measured on a Bruker 300-MHz instrument. All chemical shifts are reported relative to Me$_4$Si, and all isotropic shifts are relative to square-planar, diamagnetic Ni(OEPR$_2$).[25] Most spectra were collected with use of 32K data points, a 14-μs pulse, and a delay time of 2 s. Under these conditions no saturation of signal occurred. Deuterated solvents were purchased

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Table I. ^{1}H NMR Chemical Shifts (ppm),[a] Isotropic Shifts (ppm),[b] and Line Widths (Hz)[c] for Co(OEPR$_2$) in CDCl$_3$, 293 K

compd	5-H	10-H	α-CH$_2$		β-CH$_3$	51-H	52-H
Co(OEPMe$_2$)	*30.32*	*20.28*	*11.02*	*9.06*	*6.41*	*−26.41*	...
			9.90	*8.82*	*5.50*		
	26.4	13.4	8.6	6.6	5.3	−28.6	...
			7.5	6.4	4.4		
	(38)	(33)	(31)	(31)	(20)	(89)	
Co(OEPEt$_2$)	*28.00*	*20.77*	*10.56*	*8.77*	*5.83*	*−31.48*	*−8.47*
			9.54	*7.98*	*5.54*		
	24.2	14.1	8.2	6.4	4.7	−34.2	−9.6
			7.1	5.6	4.4		
	(55)	(45)	(30)	(30)	(21)	(161)	(85)
Co(OEPPr$_2$)	*24.61*	*20.73*	*9.82*	*7.04*	*5.37*	*−40.47*	*−9.03*
			9.70	*6.50*	*4.96*		
	21.0	14.2	7.4	4.6	4.3	−44.0	−10.3
			7.3	4.1	3.9		
	(82)	(78)	(31)	(31)	(21)	(440)	(172)
Co(OEPBu$_2$)	*26.71*	*17.37*	*8.44*[e]	*6.56*	*5.13*	...	*−12.71*
				5.89	*3.98*		
	22.8	10.8	6.0	4.1	4.1	...	−14.3
				3.5	2.9		
	(145)	(112)	(59)	(36)	(21)		(278)
Co(OEP)[d]		19.0	3.55		4.55		

[a] The chemical shifts are listed in italics and are relative to Me$_4$Si. [b] All isotropic shifts are relative to the corresponding Ni(OEPR$_2$) resonances in CDCl$_3$ (293 K).[25] A positive isotropic shift means a shift to *lower* field. [c] The line width in Hz is given in parentheses. For the α-CH$_2$ resonance, as in Co(OEPMe$_2$), four separate signals are observed, each with a line width of 31 ± 1 Hz. The line widths of all other α-CH$_2$ and β-CH$_3$ signals are reported similarly. [d] Data taken from ref 19. [e] This signal is due to two α-CH$_2$ resonances that are accidentally isochronous.

from Merck and used without further purification.

The ESR spectrum was measured on a Varian X-band, E-line spectrometer operating at 9.25 GHz.

Results and Discussion

The cobalt porphodimethenes **1–4** were obtained by treatment of the metal-free porphodimethenes, H$_2$(OEPR$_2$), with dicobalt octacarbonyl and iodine in boiling toluene. They were fully characterized by elemental analysis and UV/vis, IR, and mass spectroscopy (see Experimental Section). The complexes are partly dehydrogenated and partly decomposed when dissolved in hot, polar solvents or when adsorbed to chromatographic stationary phases. However, purification by chromatography in the absence of oxygen is possible.

A representative proton NMR spectrum, that of Co(OEPBu$_2$), is shown in Figure 1. Except for the 5,15-H and 10,20-H protons all other signals could be assigned from their relative areas and from comparisons within the series **1–4**. For all four compounds, two signals of equal area are found between 30 and 15 ppm. As will be shown (vide infra), the low-field resonance results from the 5-H protons whereas the higher field resonance of this pair belongs to the 10-H protons. The chemical shifts, isotropic shifts, and line widths for **1–4** are listed in Table I.

The interpretation of these shifts shall begin with a comparison to the NMR spectra of the cobalt(II) porphyrins. Here it is believed that the ground state is ^{2}A, the unpaired spin is in d$_{z^2}$, the principal magnetic axis (z) is orthogonal to the plane of the porphyrin, and finally the isotropic shifts result principally from a dipolar coupling interaction.[19,21,22] The last conclusion seems warranted because the unpaired electron occupies the d$_{z^2}$ orbital, which is only weakly bonding. The isotropic shifts for Co(OEP) are also listed in Table I. The meso proton in Co(OEP) corresponds to 10-H in Co(OEPR$_2$). The isotropic shifts for corresponding protons in Co(OEPR$_2$) and Co(OEP) are similar in sign and magnitude. In addition the NMR spectra of the Co(OEPR$_2$) complexes exhibit the upfield signals due to the syn-axial alkyl protons. Also like Co(OEP), the Co(OEPR$_2$) complexes have no "spin isolated" protons; hence separation of contact from dipolar shift cannot be accomplished quantitatively. However, calculations of relative dipolar shifts and relative line widths based upon reasonable geometries can still lead to valuable insights on the structure of these molecules in solution if indeed the observed isotropic shifts are predominantly dipolar and nuclear relaxation occurs exclusively via a dipolar mechanism.

The dipolar shift $(\Delta H/H)_{\mathrm{dip}}$ for nuclei in complexes of rhombic symmetry is given by eq 2,[14] where χ_i represents the principal components of the magnetic susceptibility, r is the proton–metal distance, θ is the angle that the vector $\vec{r}$ makes with the z axis, and Ω is the angle between the x axis and the xy projection of $\vec{r}$. In this coordinate system, the metal is at the origin. All other

$$(\Delta H/H)_{\mathrm{dip}} = \frac{1}{3N}\left\{\left[\chi_z - \frac{1}{2}(\chi_x + \chi_y)\right]\frac{(3\cos^2\theta - 1)}{r^3} + \frac{3}{2}(\chi_x - \chi_y)\frac{\sin^2\theta\cos 2\Omega}{r^3}\right\} \quad (2)$$

symbols have their normal meanings. Although the cobalt(II) porphodimethenes have only C_{2v} symmetry, appropriate for eq 2, the ESR spectra of both Co(OEPMe$_2$) and Co(OEPBu$_2$) in toluene at 77 K are strictly axial.[13] On this basis the NMR spectra will be analyzed, assuming effective axial symmetry. The dipolar shift in molecules possessing axial symmetry is given by eq 3[14]

$$(\Delta H/H)_{\mathrm{dip}} = \frac{1}{3N}(\chi_\parallel - \chi_\perp)\left(\frac{3\cos^2\theta - 1}{r^3}\right) \quad (3)$$

and is directly proportional to the geometric factor, $G = (3\cos^2\theta - 1)/r^3$. For any two protons in a complex, $G_i/G_j = (\Delta H/H)_{i,\mathrm{dip}}/(\Delta H/H)_{j,\mathrm{dip}}$.

A second factor in the analysis are the proton line widths, $\Delta\nu_{1/2}$, which for any signal are related to the transverse nuclear relaxation time T_{2N} as follows: $\pi\Delta\nu_{1/2} = T_{2N}^{-1}$. Nuclear relaxation may occur both by dipolar and scalar mechanisms.[26] For low-spin cobalt(II), where the contact shifts and resulting hyperfine coupling constants are small and T_{1e}, the electron relaxation rate, is relatively fast, nuclear relaxation will occur only via the dipolar mechanism.[20] For complexes possessing magnetic anisotropy, the relevant equation for the nuclear relaxation time has been derived by Sternlicht.[27] When the contact interaction is small, only the first term is used and this is presented in eq 4. The magnetic

$$T_{2N}^{-1} = \frac{2\gamma_I^2\beta^2 S(S+1)}{3r^6}[\bar{g}^2 + g_\parallel^2\cos^2\theta + g_\perp^2\sin^2\theta]\tau_c \quad (4)$$

anisotropy is expressed in terms of $g_\perp$ and $g_\parallel$; τ_c is the electron spin–nuclear spin correlation time, and θ and r were defined previously. The remaining symbols have their normal meaning.

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The line width for any proton is proportional to the line width factor L where

$$L = (\bar{g}^2 + g_{\parallel}^2 \cos^2 \theta + g_{\perp}^2 \sin^2 \theta)/r^6 \qquad (5)$$

and for any two protons in a complex, $L_i/L_j = (\Delta\nu_{1/2})_i/(\Delta\nu_{1/2})_j$. The choice of $g_{\parallel}$ and $g_{\perp}$ is problematic. For polycrystalline Co(OEPBu$_2$) at 15 K, we find the ESR spectrum to be axial to first order with $g_{\parallel} = 2.05$ and $g_{\perp} = 3.46$. In toluene at 77 K the values are $g_{\parallel} = 2.02$ and $g_{\perp} = 2.60$.[13] La Mar and Walker[19,28,29] and Williams[21] have discussed thoroughly the magnetic anisotropy of cobalt(II) porphyrins in various solvent media. It is apparent that the magnetic anisotropy for cobalt(II) porphyrins at room temperature as *inferred* from the NMR spectra is clearly larger than that measured by ESR in solvent glasses at 77 K. Also the effective room-temperature anisotropy in solution is believed to be closer in magnitude to that in a polycrystalline solid.

For Co(OEPR$_2$) we shall use $g_{\parallel} = 1.8$ and $g_{\perp} = 3.5$ in calculations involving eq 3 and 4. This slightly larger anisotropy is indicated from the magnitude of the shifts in Table I.

For protons having the same value of τ_c in any particular Co(OEPR$_2$) complex, a comparison of relative line widths can yield information about metal–proton distances. If the protons being compared have similar values of $\cos^2 \theta$, as will be shown for 5-H and 10-H, then the ratio $(\Delta\nu_{1/2})_i/(\Delta\nu_{1/2})_j = (r_j/r_i)^6$ and the exact choice of θ, $g_{\parallel}$ and $g_{\perp}$ is not at all critical.

For the calculation of geometric factors, G, and line width factors, L, the known structures of Ni(OEPMe$_2$)[12a] and Co(OEPBu$_2$)NO[12f] were taken as a starting model with averaged pyrrole ring bond distances and angles being used. The cobalt atom, 5-C and 10-C atoms, and related protons 5-H, 10-H, 51-H, and 52-H were varied in position relative to the plane of the four pyrrole nitrogens in order to assess the change in geometry upon the calculated line width factors and geometric factors. Folding of the macrocycle along the 10-C to 20-C axis and ruffling of the pyrrole rings were also used. Geometric factors and line width factors were calculated by computer for all protons except β-CH$_3$. When bond rotation occurred, these factors were calculated by computer for 1° rotation intervals and then averaged. The principal magnetic axis was chosen to be orthogonal to the tetraaza plane. Any other choice, either the Co–N axes or their bisectors, resulted in geometric factors inconsistent with the observed pattern of isotropic shifts.

Our approach has been to find a geometry for Co(OEPR$_2$) for which there is reasonable agreement between experimental and calculated line width ratios and isotropic shift ratios. More reliance is placed upon relative line widths then isotropic shifts since the latter have a small but unknown contribution from a contact interaction. Naturally one specific set of parameters (bond distances, angles) cannot be valid for all four compounds **1**–**4**. But if only minor structural changes occur within the series, then it is still possible to extract useful structural information about the conformation of these molecules in solution. In our model, the cobalt atom was placed 0.06 Å above the tetraaza plane in the direction of the syn-axial substituents and 1.95 Å from the pyrrole nitrogens. The 5,15-C atoms were placed 3.35 Å from cobalt and 1.00 Å above the tetraaza plane, while the 10,20-C atoms were positioned 3.32 Å from cobalt and 0.92 Å below the tetraaza plane. A 40° dihedral roof angle and 24° pyrrole ring ruffling were used.[30]

5,15-H and 10,20-H Protons. With use of Co(OEPMe$_2$) as an example, the two resonances at 30.32 and 20.08 ppm are assigned to the 5-H and 10-H protons, respectively. The ratio of line widths is 1.15:1 with the downfield resonance being broader. If the downfield resonance is 5-H, the isotropic shifts would be 26.35 and 13.41 ppm for 5-H and 10-H, respectively. If the assignments are reversed, the 5-H and 10-H isotropic shifts would become 16.11 and 23.65 ppm, respectively. For all reasonable geometries that can be proposed, we have calculated that the geometric factor for 5-H is always larger than that of 10-H and that 5-H is closer to cobalt.

Table II. Geometric Factors and Line Width Factors for Co(OEPMe$_2$) and Co(OEPBu$_2$)

proton	$\langle r \rangle^a$	L^b	$\Delta\nu_{1/2}$	G^b	$(\Delta H/H)_{\text{iso}}{}^b$
		Co(OEPMe$_2$)			
5-H	4.33	10.0	10.0	10.0	10.0
10-H	4.41	9.1	8.7	7.0	5.1
51-H	3.97	22.6	23.4	−11.7	−10.8
α-CH$_2$ (5-C)^c	6.00	0.15	0.82	0.42	0.28, 0.33
α-CH$_2$ (10-C)	5.97	0.15	0.82	0.35	0.25, 0.24
		Co(OEPBu$_2$)			
5-H	4.26	10.0	10.0	10.0	10.0
10-H	4.41	7.8	7.7	6.1	4.7
52-H	4.71	20.1	19	−10.2	−6.3
α-CH$_2$ (5-C)	6.00	0.14	0.41	0.38	0.26
α-CH$_2$ (10-C)	5.97	0.14	0.25	0.31	0.18, 0.15

^{a} $\langle r \rangle$ is the metal–proton distance averaged over all rotations. ^{b} All values are relative to 10.0 for 5-H. ^{c} α-CH$_2$ (5-C) means the α-CH$_2$ proton adjacent to 5-C.

If the isotropic shifts are predominantly dipolar in origin, then the downfield resonance of this pair should be assigned to 5-H consistent with its larger calculated geometric factor and shorter distance. In Table II are listed geometric factors, line width factors, and distances in our geometric model for Co(OEPMe$_2$) and Co(OEPBu$_2$). With use of the former as an example, the calculated geometric factor ratio 5-H:10-H is 1.43:1. This is smaller than the ratio of isotropic shifts and could imply that 5-H has a positive contact shift contribution whereas 10-H has a negative contact shift contribution. However, since neither the sign nor relative magnitudes of the contact shifts can be ascertained, one can at best only qualitatively compare the geometric factor ratios with isotropic shift ratios. In this regard, the geometric factor ratio calculated from a model geometry is quite reasonable. The ratio of observed 5-H/10-H isotropic shifts in the series Co(OEPR$_2$) vary from 2.11:1 to 1.48:1. This variation undoubtedly is due to variations in geometry which affect both contact and dipolar shifts.

In contrast, the line widths are more suitable for comparison if τ_c values are identical for the protons being compared. This has been confirmed for 5-H and 10-H from plots of log $\Delta\nu_{1/2}$ vs. $1/T$ (vide infra). For Co(OEPMe$_2$) our geometrical model predicts a line width ratio of 1.10:1 in close agreement with the experimental value of 1.15:1. Because $\cos^2 \theta$ is small for both 5-H and 10-H, the term $\bar{g}^2 + g_{\parallel}^2 \cos^2 \theta + g_{\perp}^2 \sin^2 \theta$ in eq 4 is nearly identical for both protons. Thus magnetic anisotropy has minimal effect upon line width calculations. Also as seen in Table II, the agreement between calculated and observed 5-H/10-H line width ratios is very good.

In an examination of the isotropic shift and line width trends in the series **1**–**4** a few comments are warranted. First, the observed line width ratio $(\Delta\nu_{1/2})_{5\text{-H}}/(\Delta\nu_{1/2})_{10\text{-H}}$ varies from 1.15 to 1.29. This should reflect minor changes in geometry and metal–proton distances within the series. Second, for a given proton—either 5-H or 10-H—the line width increases markedly as R increases in size. While this increase in $(\Delta\nu_{1/2})_{5\text{-H}}$ or $(\Delta\nu_{1/2})_{10\text{-H}}$ could reflect a systematic increase in $1/r^6$, we suspect that were this true, a concomitant increase in $(\Delta H/H)_{\text{iso}}$ would be observed. This does not occur. Most likely τ_c is increasing in the series **1**–**4** and this affects only the line widths.

Axial Protons: 51-H and 52-H. With use of Co(OEPMe$_2$) again as an example, the 51-H resonance, the broadest signal by far in the NMR spectrum, is found upfield at −26.4 ppm. Its isotropic shift is −28.6 ppm, and its line width is 89 Hz. For geometric factor calculations, it was first assumed that the 5-C to 51-C bond is vertical (collinear with the z axis). The geometric factor obtained for 51-H is approximately 50% that of 5-H.[31] Furthermore, in this geometry the line width for 51-H is calculated to be only 90% that of 5-H whereas it should be more than twice

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[28] Walker, F. A. *J. Am. Chem. Soc.* **1970**, *92*, 4235.

[29] Walker, F. A. *J. Magn. Reson.* **1974**, *15*, 201.

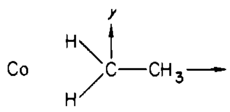
[30] For a precise definition of "dihedral roof angle" and "ring ruffling", see ref 12a.

as great.[31] If the carbon atom 5-C is moved (simple translation along x, y, or z), the relative geometric factor and line width factor change only slightly for 51-H compared to that for 5-H. The only way both the 51-H line width and isotropic shift can be drastically increased is by bending the 5-C to 51-C bond from a vertical position at least 10–15° inward toward Co. The calculated geometric and line width factors for 51-H at 15° are listed in Table II. In this latter model the dipolar shift ratio 51-H:5-H is predicted to be −1.17:1 and the relative line widths 2.26:1. The latter should be compared to the observed line width ratio of 2.34:1. Most significantly, the bond vector between 5-C and 51-C in the related Ni(OEPMe$_2$) is canted 13° toward Ni as shown by the X-ray structural determination of Scheidt.[12a] Thus there appears to be a direct parallelism between the solid-state structure of Ni(OEPMe$_2$) and the solution conformation of Co(OEPMe$_2$).

The 52-H resonance is also found upfield from Me$_4$Si at −12.71 ppm in Co(OEPBu$_2$). The isotropic shift is −14.3 ppm, and the line width is 278 Hz. As with 51-H, both G and L for 52-H are extremely sensitive to the orientation of the 5-C to 51-C bond axis.[32] We have found that L best matches the experimental line width when the aforementioned bond vector is bent in from a vertical position by 2–3° in the direction of Co. The agreement between L and $\Delta\nu_{1/2}$ is shown in Table II. There are two comparable compounds, Fe(OEPBu$_2$)OH[12e] and Co(OEPBu$_2$)NO,[12f] for which crystal structures are known. In both cases, the bending angle is 2–3°. Since a *tert*-butyl group is so much more bulky than a methyl group, it is impossible for the former to bend in 15°.

It should be noted that, with free rotation of the *tert*-butyl group, 52-H comes very close to cobalt. In our geometric model 52-H at its nearest approach is only 2.3 Å from cobalt and 26° off the z axis. There undoubtedly must be some direct overlap with d_{z^2} and a resulting downfield contact shift. When the calculated relative value of G is compared with the observed relative isotropic shift, a considerable discrepancy is discerned as shown in Table II. The dipolar shifts for 52-H and 5-H should be roughly equal in magnitude; thus a dipolar shift of approximately −23 ± 4 ppm might be expected. The observed isotropic shift is −14.3 ppm and suggests the presence of a substantial contact contribution. A *very rough* estimate of the contact shift at 52-H can be obtained by using the effective **g**-tensor anisotropy ($g_\parallel = 1.8$, $g_\perp = 3.5$), the calculated geometric factor (-0.0121 Å^{-3}), and the relationship $\chi_i = (\beta^2S(S+1)g_i^2)/3kT$. A dipolar shift of −19 ppm is calculated from eq 3. The contact shift for 52-H is then 5 ppm.[33] A second consequence of this close approach of 52-H to cobalt is the very broad signal for 52-H in **4**. Our model predicts large values of both $\langle r\rangle$ and L for 52-H—a seeming contradiction if $L \propto 1/r^6$. But when 52-H comes very close to cobalt, $1/r^6$ becomes disproportionately large and contributes greatly to $\langle 1/r^6\rangle$. Thus 52-H has the broadest signal in the spectrum of **4** even though it is on average more distant from cobalt than 5-H or 10-H.

Having developed a model for the 51-H and 52-H resonances, we now consider the changes in isotropic shift and line width for these axial protons in the series Co(OEPR$_2$). First, it should be noted that isotropic shifts and line widths for 51-H and 52-H increase serially for **1**–**4**. This change in line width is in part due to an increase in τ_c from **1** to **4** as previously proposed. However, this cannot account for the observed increase in $(\Delta H/H)_{\rm iso}$ for 51-H and 52-H in the series. A second factor may also contribute here. If one considers the rotation of the syn-axial alkyl groups about the 5-C to 51-C bond axis, it is apparent from molecular models that steric interactions occur between the CH$_3$ group (52-H) and the pyrrole ring.[34] When R = C$_2$H$_5$, i-C$_3$H$_7$, the preferred orientation should be that which keeps CH$_3$ away from the interior of the porphodimethene. This is illustrated for R = C$_2$H$_5$ with a projection down the z axis perpendicular to the tetraaza plane:



Although rotation about the 5-C to 51-C bond is fast on the NMR time scale, not all rotamers need be equally populated. Thus for the series **2**–**4**, the 52-H protons will spend the least time near Co when R = C$_2$H$_5$, in order to reduce steric repulsions, and the most time near Co in **4** when R = C(CH$_3$)$_3$. Since the geometric factor increases greatly as 52-H moves close to cobalt, the isotropic shift (mainly dipolar) for 52-H will increase in magnitude as follows: **2** < **3** < **4**. this is the observed trend of isotropic shifts.[35]

A similar argument prevails for the 51-H protons, which preferentially should spend more time closer to cobalt in the order **1** < **2** < **3**. The largest 51-H isotropic shift is expected for **3**, and this is observed. The line widths for 51-H and 52-H follow the same trend as their respective isotropic shifts for exactly the same reason: namely, the line width increases with decreasing proton–metal distance.

α-CH$_2$ and β-CH$_3$ Protons. There are two sets of methylene protons: those proximal to 5-C and those proximal to 10-C. In each set the geminal CH$_2$ protons are diastereotopic and the resonances should be anisochronous. Thus four signals are observed in the NMR spectra of the complexes **1**–**3** ranging from 5 to 11 ppm. For Co(OEPBu$_2$) at 293 K the two low-field resonances are accidentally isochronous, but at lower temperature these separate. The anisochronism of the geminal methylene protons is a consequence of the axial asymmetry in the porphodimethene ligand. A similar effect is observed in the NMR spectra of metallooctaethylporphyrins of formula M(OEP)L, where the axial ligand L is the source of axial asymmetry.[36] As expected, there are also two β-CH$_3$ resonances in each Co(OEPR$_2$) ^{1}H NMR spectrum. Both the α-CH$_2$ and β-CH$_3$ chemical shifts and isotropic shifts are listed in Table I. Only by selective deuteration can the α-CH$_2$ and β-CH$_3$ resonances definitively be assigned. However, by means of decoupling experiments we have been able to tell which pair of α-CH$_2$ resonances are geminal and which β-CH$_3$ and α-CH$_2$ resonances are coupled together. With compound **4** a strong decoupling RF field was applied to the α-CH$_2$ signal at 8.44 ppm. The high-field β-CH$_3$ resonance (3.98 ppm) became noticeably narrower, from a half width of 18 to 14 Hz, while the low-field β-CH$_3$ resonance was unchanged. Its trace was identical with that in the nonirradiated spectrum. Irradiation of the α-CH$_2$ resonance at 6.56 or 5.89 ppm produced no effect on the high-field β-CH$_3$ resonance and at most 1-Hz narrowing of the low-field β-CH$_3$ signal. We conclude that the two low-field α-CH$_2$ resonances, accidentally isochronous in **4**, are from one geminal pair, while the two high-field α-CH$_2$ resonances belong to the other geminal pair.

Assuming again that the isotropic shifts are principally dipolar, we can calculate geometric factors and line width factors and attempt to determine which geminal pair is adjacent to 5-C and which is adjacent to 10-C. Our geometric model for the α-CH$_2$ calculation is based upon the Ni(OEPMe$_2$) and Co(OEPBu$_2$)NO crystal structures. A 40° roof angle and 24° pyrrole ring ruffling were assumed as previously mentioned. The choice of values for these angles is not particularly crucial for the α-CH$_2$ calculation. What seems certain is that the α-CH$_2$ group adjacent to 5-C will have the larger dipolar shift. If the contact shift contribution is very small, then the downfield pair of α-CH$_2$ resonances belong

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(31) For this geometry, $G = -4.9$ and $L = 9.3$, both relative to 10.0 for 5-H. Compare these to the experimental values listed in Table II.

(32) For angles of 0 and 5°, the values of G and L for 52-H relative to 5-H are as follows: 0°, $G = 8.46$, $L = 15.3$; 5°, $G = 11.4$, $L = 24.4$. These numbers are to be compared with the observed values of relative isotropic shift and relative line width as listed in Table II for Co(OEPBu$_2$).

(33) A similar estimate of $(\Delta H/H)_{\rm con}$ for 5-H and 10-H in Co(OEPBu$_2$) can be made. The numbers are +4 and −1 ppm, respectively.

(34) The "CPK Atomic Models", Ealing Corp., were used.

(35) For 52-H the geometric factor, G, undergoes a change in sign with rotation. It occurs as this methyl group moves clockwise about the 5-C to 51-C axis from $+y$ to $-y$ (see above diagram). Over this 180° semicircle $\langle G\rangle \simeq 0$. The dipolar shift for 52-H is a consequence only of rotation (clockwise) from $-y$ to $+y$ where these protons become very close to cobalt.

(36) Dolphin, D. *J. Magn. Reson.* **1976**, *23*, 211.

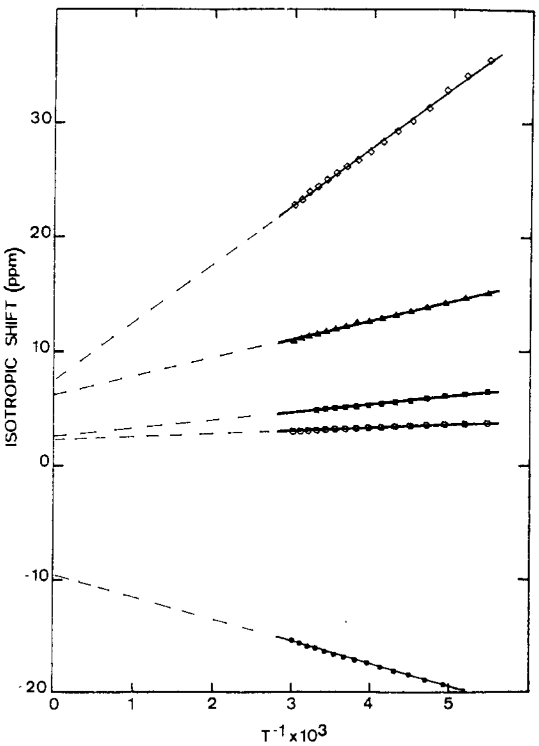

Figure 2. Curie plot for proton resonances of Co(OEPBu$_2$) in toluene-d_8: (◇) 5-H; (▲) 10-H; (■) α-CH$_2$; (○) β-CH$_3$; (●) 52-H.

to the geminal pair adjacent to 5-C. Relative geometric factors, relative line width factors, and average distances are listed in Table II. Very little difference in line width is predicted for the α-CH$_2$ resonances, and this is observed.

The spread within a geminal set of α-CH$_2$ resonances varies from 0 to 1.2 ppm in the four compounds. If the α-CH$_2$ groups are rotating freely and all rotamers are equally populated, then the two protons of a geminal pair will have identical geometric factors and dipolar shifts. The difference then in isotropic shift for this pair would result from differing contact shifts. On the other hand, unequal population of rotamers would signify a difference in dipolar shifts for a geminal pair. Most likely the difference in isotropic shifts in a geminal pair reflects the latter.

The α-CH$_2$ protons are approximately 6 Å from cobalt and should show rather narrow resonances in the NMR spectra. However, the observed line widths are substantially larger than that predicted from our geometrical model. In Co(OEPMe$_2$), for example, the α-CH$_2$ line width, 30 Hz, is 5 times greater than predicted. This broadening will be discussed in the next section.

Geometric modeling of the β-CH$_3$ isotropic shifts was not attempted because of the small shifts and the high degree of rotational freedom. However, these protons should be sufficiently distant from cobalt so that the observed isotropic shifts are purely dipolar.

Temperature Dependence of the Isotropic Shifts and Line Widths. The isotropic shifts and line widths of Co(OEPBu$_2$) were measured from 183 to 333 K in toluene-d_8 because of solubility considerations and the extended liquid range of this solvent. The isotropic shifts are plotted vs. $1/T$ in Figure 2. Straight-line behavior is observed rigorously for all protons. This linearity means that $\chi_\parallel - \chi_\perp$ is independent of temperature and that no significant structural changes, either aggregation or axial ligation, occur over the temperature range. Also observed for all protons are non-zero intercepts from 6 to 10 ppm at $1/T = 0$. This has been attributed in part to a second-order Zeeman (SOZ) perturbation,[37] which causes a linear deviation from simple Curie behavior. However, the magnitude of this SOZ contribution cannot be ascertained without knowing the principal magnetic susceptibilities.

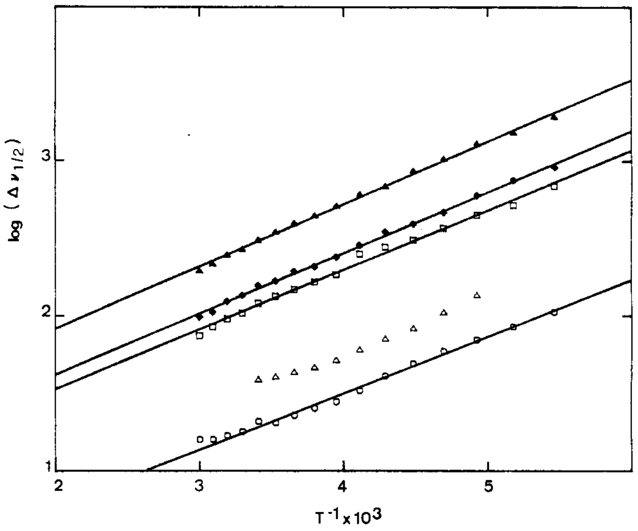

Figure 3. Arrhenius plot of log (line width) vs. reciprocal temperature for Co(OEPBu$_2$) in toluene-d_8: (▲) 52-H; (◆) 5-H; (□) 10-H; (△) α-CH$_2$; (○) β-CH$_3$.

The ^{1}H NMR temperature dependence of only one cobalt(II) porphyrin, Co(TTP) in toluene-d_8, has been similarly studied. The Curie plot for this compound is nonlinear for all protons.[19] This has been ascribed to a changing axial interaction, perhaps aggregation effects, which become more pronounced at low temperature. However, for each proton in Co(TTP) the three high-temperature points did appear to fall on a straight line, which had a zero intercept at $1/T = 0$. Thus Co(OEPBu$_2$) and Co(TTP) have different solution behaviors, which is likely due to the rooflike structure of the cobalt porphodimethene and the subsequent change in its Lewis acid/base properties.

The line width of the proton resonances are also temperature dependent and increase with decreasing temperature. Because electron relaxation is known to be rapid for low-spin cobalt(II) porphyrins,[19] the correlation time, τ_c, should be equal to T_{1e} for **1**–**4**. The temperature dependence of τ_c is given by[38]

$$\tau_c = \tau_c^0 \exp(\pm E_a/RT)$$

where E_a is the activation energy for the motions governing τ_c. Since T_{2N}^{-1} is proportional to τ_c, a plot of log $\Delta\nu_{1/2}$ vs. $1/T$ should be linear. This is observed for the 5-H, 10-H, 52-H, and β-CH$_3$ protons in Co(OEPBu$_2$) as seen in Figure 3. Furthermore, because the lines are parallel, these nuclei must have identical relaxation rates and mechanisms. With use of the 5-H half-width in **4**, τ_c is calculated from eq 4 to be 2×10^{-12} s. This is substantially faster than the tumbling time estimated for metalloporphyrins,[39] 5×10^{-10} s, and indicates that $\tau_c = T_{1e}$ for these protons.

Examination of the α-CH$_2$ log $\Delta\nu_{1/2}$ plot[40] in Figure 3 yields a different conclusion for these particular protons. First, the plot shows mild curvature, indicative that rotation of the CH$_2$ group may be sterically hindered as also suggested by space-filling molecular models.[34]

Also, the line widths of the α-CH$_2$ protons (see Table I) are essentially invariant and are broader than expected throughout the series **1**–**4**. This could imply that the line widths are determined by the rotational motion of the sterically hindered C$_2$H$_5$ groups and that this motion is slower than T_{1e}. However, a more plausible explanation may be related to the underlying multiplet structure of the α-CH$_2$ resonance. In diamagnetic Ni(OEPR$_2$)[25] the CH$_2$CH$_3$ group is an ABX$_3$ system where $J_{AX} = J_{BX} = 7$ Hz

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(37) Horrocks, W. D. *Mol. Phys.* **1974**, *27*, 993.

(38) Dweck, R. "Nuclear Magnetic Resonance in Biochemistry"; Clarendon Press: Oxford, 1973; pp 176–190.

(39) La Mar, G. N.; Walker, F. A. *J. Am. Chem. Soc.* **1973**, *95*, 6950.

(40) Only for one α-CH$_2$ resonance were we able to measure a reasonable number (10) of line widths for the log ($\Delta\nu_{1/2}$) plot. For the other three α-CH$_2$ protons, overlapping of signals at many temperatures interfered with the line width measurements.

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and J_{AB} = 14 Hz. If in the paramagnetic Co(OEPR$_2$) there is not complete collapse of the ABX$_3$ multiplet structure, then the lines will be broader than calculated from eq 5 and possibly equal in line width throughout the series **1**–**4**. Thus it is debatable as to what effect, if any, "hindered rotation" of α-CH$_2$ has upon the NMR spectra of these porphodimethenes.

Similar steric crowding of the α-CH$_2$ groups has also been proposed for OEP complexes. La Mar and Walker alluded to the "severely restricted rotation" of the α-CH$_2$ groups in [Fe(OEP)(Im)$_2$]Cl because a plot of $(\Delta H/H)_{\text{iso}}$ was linear with T for these protons.[41] However, other compounds, for example Fe(OEP)[42] and [Fe(OEP)(pip)$_2$]Cl,[43] exhibit linear $(\Delta H/H)_{\text{iso}}$ vs. T^{-1} plots for α-CH$_2$. Thus there is also ambiguity for OEP complexes.

Base Addition to Co(OEPR$_2$). Because the dialkylporphodimethenes have an intrinsic asymmetry, one can in principle determine whether axial coordination of base occurs from the top (syn-axial) or bottom (anti-axial). This will be illustrated for the addition of 1-methylimidazole (1-MeIm) to Co(OEPBu$_2$). When small amounts of 1-MeIm in toluene-d_8 are added to Co(OEPBu$_2$), the porphodimethene proton resonances broaden quickly and coalesce toward the diamagnetic region. Axial ligand exchange is rapid on the NMR time scale, and the resonance positions are a mole fraction average of that in Co(OEPBu$_2$) and Co(OEPBu$_2$)·1-MeIm. The diminished isotropic shifts in the five-coordinate species have been attributed to a smaller magnetic anisotropy in square-pyramidal cobalt(II); the line broadening has been explained by a decrease in T_{1e} upon axial addition.[19]

If one assumes that upon axial addition no major structural changes occur other than the metal moving out of the tetraaza plane toward the 1-MeIm, then one can compare relative proton line widths of Co(OEPBu$_2$) as a function of added ligand and obtain useful structural information. As an example, the line widths of 5-H and 10-H in Co(OEPBu$_2$) were monitored as a function of added 1-MeIm. In all porphodimethenes 5-H sits above the tetraaza plane (+Z coordinate) whereas 10-H is located below the tetraaza plane (−Z coordinate). For Co(OEPBu$_2$) axial coordination can occur only from the bottom since the top side is blocked effectively by the bulky syn-axial *tert*-butyl groups. Upon coordination of base, the cobalt atom will move downward, closer to 10-H but more distant from 5-H. Thus one expects $(\Delta\nu_{1/2})_{5\text{-H}}/(\Delta\nu_{1/2})_{10\text{-H}}$ to decrease as a function of added base. Were axial coordination to occur from the top side, the aforementioned ratio would increase instead.

Experimentally when 1-MeIm in toluene-d_8 was added in small increments to a solution of Co(OEPBu$_2$) in toluene-d_8, the aforementioned line width ratio *decreased* as expected from a initial value of 1.28 to 1.09, at which point the lines became too broad for precise measurement. This suggests axial coordination from the bottom, unhindered side. For 100% adduct formation with cobalt displaced 0.10 Å below the tetraaza plane, as in Co(OEPBu$_2$)NO, our geometrical model predicts $(\Delta\nu_{1/2})_{5\text{-H}}/(\Delta\nu_{1/2})_{10\text{-H}} = 0.851$. Addition of 1-MeIm to Co(OEPMe$_2$) yielded equivocal results with no discernable trend in $(\Delta\nu_{1/2})_{5\text{-H}}/(\Delta\nu_{1/2})_{10\text{-H}}$. Since Co(OEPMe$_2$) can coordinate from either top or bottom, both processes may occur concurrently with near-equal probability.

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Registry No. **1**, 97805-52-2; **2**, 97732-92-8; **3**, 97732-93-9; **4**, 97805-53-3; Co$_2$(CO)$_8$, 10210-68-1.

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(42) Mispelter, J.; Momenteau, M.; Lhoste, J. M. *Mol. Phys.* **1977**, *33*, 1715.

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Characterization of Bis(tripeptido)nickelate(III) Complexes in Aqueous Solution

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Addition of excess tripeptide (L$^-$) to solutions of (tripeptido)nickel(III), Ni$^{\text{III}}$(H$_{-2}$L), gives bis(tripeptido)nickelate(III) complexes. In the initial reaction [Ni$^{\text{III}}$(H$_{-2}$L)L]$^-$ forms, but it is a transitory species that rapidly loses a proton to give [Ni$^{\text{III}}$(H$_{-2}$L)(H$_{-1}$L)]$^{2-}$, a complex with five nitrogens coordinated to nickel. This five-nitrogen complex is relatively stable from pH 6 to 11. It converts to a six-nitrogen tetragonally elongated complex, [Ni$^{\text{III}}$(H$_{-2}$L)$_2$]$^{3-}$, above pH 11. The bis complexes of G$_3^-$ are 10^3–10^6 times slower to undergo base-catalyzed redox decomposition than are the corresponding mono complexes of nickel(III). The bis(glycyl-L-alanylglycinato) complex, [Ni$^{\text{III}}$(H$_{-2}$GAG)(H$_{-1}$GAG)]$^{2-}$, dissociates in acid to form Ni$^{\text{III}}$(H$_{-2}$GAG) with a first-order rate constant of 34 s^{-1} (25.0 °C) from pH 1.5 to 3.5. Electron-transfer reactions of the bis complexes occur via outer-sphere mechanisms, and the bis(tripeptido)nickelate(II) complex produced dissociates rapidly to Ni$^{\text{II}}$(H$_{-2}$L)$^-$. The reduction potentials of the bis complexes are estimated to be less than 0.24 V (vs. NHE).

Introduction

Deprotonated oligopeptide complexes of nickel(III) have been shown to be moderately stable in aqueous media.[1,2] Electron paramagnetic resonance studies[3-5] indicate that nickel(III)-tripeptide complexes have tetragonally elongated geometry with water molecules in the axial sites (z axis)[6] and with the unpaired electron in the d$_{z^2}$ oribtal. The nature of the tripeptide ligand has relatively little effect on the reduction potential of the mono complexes. Values of $E°'$ vary from 0.80 to 0.89 V (vs. NHE) for different tripeptide complexes.[2]

Recently, nickel(III) has been found in several nickel-containing bacteria.[7-11] Hydrogenase from *Desulfovibrio gigas* reportedly contains one nickel(III) per enzyme molecule and has a reduction

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