This oversimplified model seems qualitatively correct for these complexes and recent work in this laboratory on tris-dtc complexes of V(III) and Mn(III) is also qualitatively consistent.[63] This model also requires that all of the complexes invert by the trigonal twist mechanism. This pathway has not been proved for the Co(III) and Rh(III) tris-dtc complexes but is the most likely mechanism (*vide supra*).

The observation that $Co(dtc)_3$ inverts faster than $Rh(dtc)_3$ is consistent with the general trend found for transition metals, *i.e.*, the rate of metal-centered rearrangement decreases on descending a group. Work in this laboratory has recently yielded the result that $Fe(dtc)_3$ complexes racemize faster than the $Ru(dtc)_3$ analogs, and both by the trigonal twist mechanism.[2,64] This trend is consistent with the order in rate of isomerization found for H_2ML_4[65] and $HM(PF_3)_4^-$[66] type complexes where L = phosphine or phosphite and where Fe > Ru and Co > Rh > Ir, respectively. Other examples of this order in rate are for $M(tfac)_3$ complexes where Co(III) > Rh(III)[50b] and Fe(III) > Ru(III);[50a] and for $M(\alpha\text{-RT})_3$ where Co(III) > Rh(III).[5] In cases where the trigonal twist mechanism is operative, the ΔLFSE argument can be applied. The size of ΔLFSE depends on *Dq*. Larger ligand field strengths will increase ΔLFSE and hence raise the activation energy. The value of *Dq* for the same ligand increases on descending a group. This same argument also applies for bone rupture mechanisms because the LFSE for TAP coordination increases on descending a group; hence the TAP complex becomes more stable. This behavior contrasts with the isomerization rates found for tris-β-diketonate complexes[7,50b] and tris-α-R-tropolonate complexes[5] of group IIIA metal ions. For these complexes the rate of isomerization increases in the order Al < Ga < In, and Al < Ga, respectively. Ligand field effects are absent here and the order parallels the order in metal ionic radius $Al^{3+} < Ga^{3+} < In^{3+}$.[5] The β-diketonate complexes presumably isomerize *via* a bond rupture mechanism[7,50b] whereas the α-RT complexes invert by a trigonal twist pathway.[5]

Acknowledgments. This research was supported in part by the donors of the Petroleum Research Fund, administered by the American Chemical Society, the Research Corporation, and the University of Minnesota Graduate School.

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Molecular Structures of Porphyrin Complexes in Solution. An ¹H Nuclear Magnetic Resonance Spectroscopic Investigation of the Interaction between 2,4,7-Trinitrofluorenone and Nickel(II) and Cobalt(II) Mesoporphyrin IX Dimethyl Esters

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Contribution from the Inorganic Chemistry Laboratory and
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Abstract: Complexes (1 : 1) formed between cobalt(II) and nickel(II) mesoporphyrin IX dimethyl ester and 2,4,7-trinitrofluorenone in $CDCl_3$ have been investigated by ¹H nmr spectroscopy. The chemical shifts of the trinitrofluorenone resonances are linearly dependent on the concentration of both cobalt(II) and nickel(II) porphyrins, and the shifts in the fully formed complexes and formation constants have been calculated. It is concluded that the shifts are caused by the ring current in the case of nickel(II) porphyrin and the ring current plus the dipolar interaction for the paramagnetic cobalt(II) porphyrin. By using the ratios of the dipolar shifts and assuming the ring current effect with cobalt(II) porphyrin is equal to that with nickel(II) porphyrin, the possible solution structures for the molecular complex have been calculated by computer methods. One family has the planes of the two components parallel at 4.0 ± 0.2 Å with complete overlap of the porphyrin and nitroarene.

Recently, there has been[2] considerable interest in the use of lanthanides as "shift reagents" though perhaps the most important aspect[3] of such work is the ability to derive detailed geometric information of the structures of lanthanide complexes in solution, making use of the assumption, justifiable in many instances, that the shift is caused primarily by the dipolar contribution.[4] In a brief communication,[5] we reported the use of cobalt(II) mesoporphyrin IX dimethyl ester to perturb the ¹H nmr spectrum of 1,3,5-

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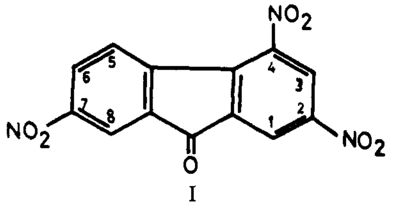
trinitrobenzene, in effect, as a shift reagent. We considered that it should be possible to develop this approach into a method of determining the *geometries* of molecular complexes in solution, if we could be assured that the principal contribution to the paramagnetic (Knight) shift was made by the dipolar term and if a reasonable way could be found of allowing for the ring-current contribution to the shift. We chose, therefore, to investigate in detail the complex formed[6] between cobalt(II) mesoporphyrin IX dimethyl ester (Co^{II}MPDE) (II) and 2,4,7-trinitrofluorenone (I) which has a relatively large formation constant in chloroform. It was considered that I was likely to retain its rigid planar structure in solution and it also has the advantage of containing a sufficient number of inequivalent protons. The interaction of Co^{II}MPDE with other nitroarenes is described[7] elsewhere.



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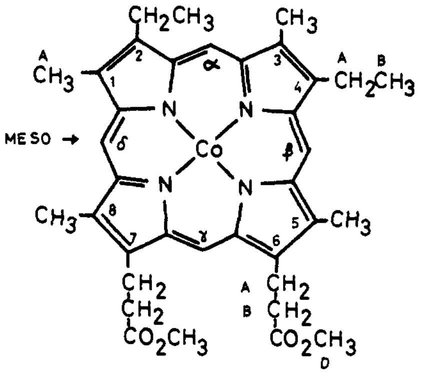

II

An associated interest in the use of Co^{II}MPDE as a probe arises from the possibility[8] of replacing iron porphyrins by their cobalt(II) analogs in heme proteins. Likewise the interaction between metal porphyrins and steroids,[9] quinones,[10] and purines[11] may be relevant to similar interactions in biological systems.

Experimental Section

2,4,7-Trinitrofluorenone was a Hopkins and Williams reagent for organic analysis and mesoporphyrin IX dimethyl ester (puriss) was supplied by Koch-Light Ltd. Deuteriochloroform, obtained from C.I.B.A. (A.R.L.) Ltd. and tetramethylsilane from B.D.H., were stored over Linde 4 Å molecular sieve. All other solvents were Analar grade.

Nickel(II) Mesoporphyrin IX Dimethyl Ester. Nickel acetate tetrahydrate (250 mg, 1 mmol) and 175 mg of mesoporphyrin IX dimethyl ester (0.3 mmol) were refluxed in glacial acetic acid (75 ml) for 30 min. The reaction mixture was allowed to cool and the crystalline precipitate was filtered off and recrystallized from chloroform–methanol following the general procedure for porphyrin esters.[12]

Anal. Calcd for $C_{36}H_{40}NiN_4O_4$: C, 66.4; H, 6.2; N, 8.6. Found: C, 66.65; H, 6.3; N, 8.4.

Cobalt(II) Mesoporphyrin IX Dimethyl Ester. This was prepared as described.[13] Since oxidation of cobalt(II) to cobalt(III), as indicated by an increased absorption at 411 nm, could have occurred during recrystallization, most experiments were carried out with the crystalline product isolated from the reaction mixture. This was thoroughly washed with glacial acetic acid, methanol, and a little peroxide-free ether and dried in an oven at 393°K and then *in vacuo*. The purity determined by absorption spectroscopy, using the known[12] extinction coefficient at 552 nm in benzene, was >99%.

Anal. Calcd for $C_{36}H_{40}CoN_4O_4$: C, 66.4; H, 6.2; N, 8.6. Found: C, 66.6; H, 6.1; N, 8.45.

Instrumental Methods. ^{1}H nmr spectra were recorded at 60 MHz using a JEOL-JNM-C6OHL spectrometer in the field sweep mode. Tetramethylsilane was used as an internal reference and field stabilization was obtained through the use of an external lock. The 220-MHz spectrum was obtained using the S.R.C. service at Runcorn. Epr spectra were recorded on a JEOL JES-3BSX spectrometer at *ca.* 9.15 GHz.

Titration Procedures. The following titration method, at constant Co^{II}MPDE concentrations, was used for the measurement of equilibrium constants and shifts in the fully formed complex. The required amount of Co^{II}MPDE was weighed into a 2-ml standard flask and made up to the mark with $CDCl_3$ and 2 μl of TMS to give solution A. The 2,4,7-trinitrofluorenone (I) was weighed out into a 1-ml standard flask and made up with standard Co^{II}MPDE solution to give solution B. Each solution (0.5 ml) was then added to separate nmr tubes using a gas-tight syringe. Solution B was taken and the resonance positions obtained as accurately as possible at 60 MHz. A small volume of the solution A was added from a gas-tight syringe and the spectrum recorded. This was repeated with various incremental additions of A. The reverse titration was carried out adding solution B, so that the measurements were made over a wide range of concentrations of I. The absorption spectra of the solutions were recorded to ensure that no oxidation of Co(II) to Co(III) had occurred. The volumetric flasks were calibrated with chloroform of known density, and by working quickly and using $CDCl_3$ which had been degassed and then saturated with nitrogen, the experiments would be carried out without significant (<2%) oxidation. Other experiments at a constant concentration of I were carried out in a method analogous to the above.

Computation. Shift and broadening ratios were calculated on an Argus 500 computer using a Fortran program. Display facilities were used for molecular orienting and origin shifting. Equilibrium constants were calculated using a KDF9 computer with an Algol program, and the Co^{II}MPDE epr spectrum was simulated by Dr. J. Boas of the University of Keele.

Results

The effects of the addition of Ni^{II}MPDE and Co^{II}-MPDE on the 60-MHz ^{1}H nmr spectrum of a solution of I in $CDCl_3$ are shown in Figures 1 and 2, respectively. Although the spectrum of I at 60 MHz is not completely first-order, an assignment was made possible by obtaining the 220-MHz spectrum: 1-H, -8.78; 3-H, -8.98; 5-H, -8.32; 6-H, -8.53; 8-H, -8.62 (± 0.01) ppm from TMS; with $J_{1,3} = 1.9$, $J_{5,6} = 8.3$, $J_{6,8} = 2.5$, and $J_{5,8} = 0.6$ (± 0.3) Hz. Figure 1 emphasizes the use of Ni^{II}MPDE as a diamagnetic shift reagent.[14] There are large shifts to high field, and as the chemical shift differences increased, the spectrum became first order. The presence of only one set of resonances indicates that the rate of exchange between free and complexed I is fast on the nmr time scale. The derived coupling

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[6] H. A. O. Hill, A. J. Macfarlane, and R. J. P. Williams, *J. Chem. Soc. A*, 1704 (1969).

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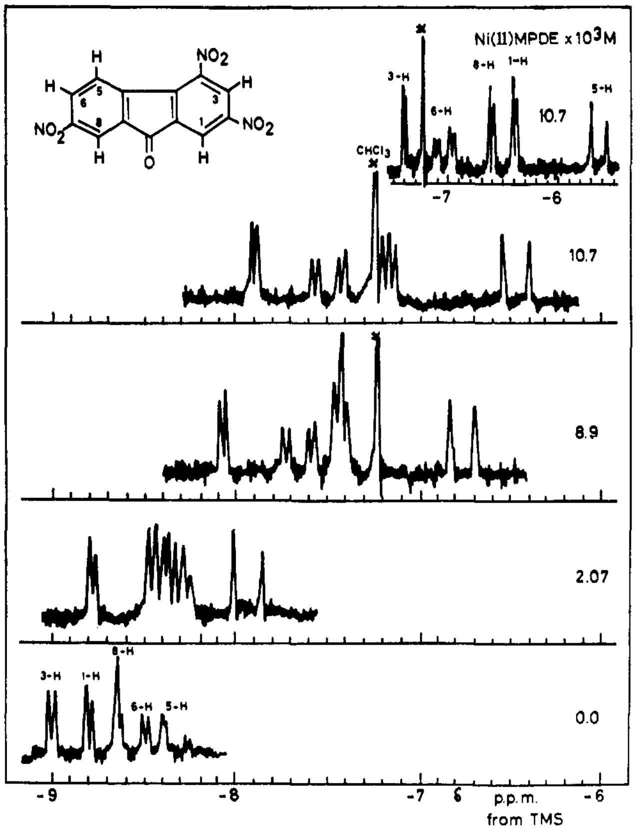

Figure 1. The effect of the addition of $Ni^{II}MPDE$ (final concentration given in the figure) on the ^1H nmr spectrum of I at 60 MHz in $CDCl_3$.

constants, $J_{1,3} = 1.9$, $J_{5,6} = 8.2$, and $J_{6,8} = 2.3$ (± 0.3) Hz were in good agreement with those derived from the 220-MHz spectrum.

The dependences of the chemical shifts of I on the $Ni^{II}MPDE$ concentration are shown in Figure 3, and the reciprocal gradients of the straight lines are given in Table I. A titration at constant $Ni^{II}MPDE$ concentration (9×10^{-4} *M*) was used to determine the formation constant and the shifts in the fully formed complex. For a 1 : 1 complex, eq 1 holds where *P* is the total porphyrin concentration, *A* is the total concentration of I, Δ is the observed shift of the resonance relative to that of the free I, and Δ_1 is the shift in the fully formed complex. A plot of ($1/\Delta$) against $A(1 - (\Delta/\Delta_1))$ was used to obtain the best value of K_1 and Δ_1.

$$1 + K_1A(1 - \Delta/\Delta_1) = K_1P\Delta_1/\Delta - PK_1 \qquad (1)$$

The gradient is $1/P\Delta_1$ and intercept $(1 + K_1P\Delta_1) + (1/\Delta_1)$. A computer program carried out a regression analysis, using a simplified calculation without the $(1 - (\Delta/\Delta_1))$ correction factor, to find Δ_1 and then an accurate calculation fitting the points to the best straight line using the principle of least squares. This procedure was applied to 5-H and 3-H but could not be used for 6-H, 8-H, and 1-H because of overlap of peaks in the spectrum. Since the reciprocal gradients are given by $(K_1\Delta_1/(1 + K_1A))$, it was possible to estimate these fully formed shifts from their ratio with respect to 5-H. They are given in Table I and labeled Δ_1(ring) since they are assumed to be caused by the porphyrin ring current.

Table I. 2,4,7-Trinitrofluorenone (0.03 *M*) Proton Shifts in the Presence of Nickel(II) Mesoporphyrin IX Dimethyl Ester in $CDCl_3$ at 298 °K

Reciprocal gradients (ppm mol^{-1} l. $\times 10^{-2}$)		Δ_1(ring),[a] ppm	K_1, l. mol^{-1}
1-H	1.53 ± 0.08	(6.7 ± 0.8)	
3-H	1.03 ± 0.07	5.0 ± 0.8	401 ± 392
5-H	1.75 ± 0.06	7.8 ± 0.4	316 ± 127
6-H	1.03 ± 0.07	(5.0 ± 0.8)	
8-H	1.33 ± 0.08	(5.8 ± 0.8)	

[a] The shifts in parentheses were estimated from the reciprocal gradient ratios with 5-H.

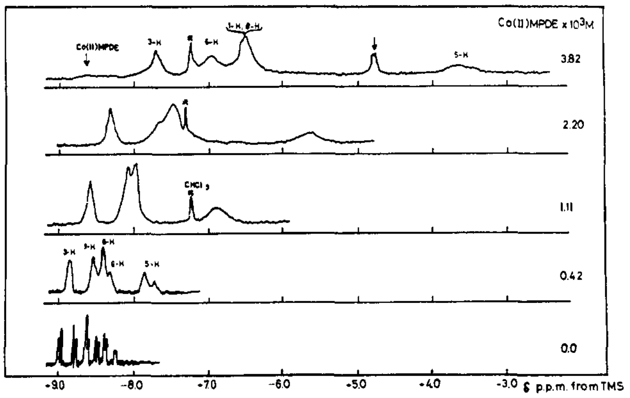

Figure 2. The effect of the addition of $Co^{II}MPDE$ (final concentration given in the figure) on the ^1H nmr spectrum of I at 60 MHz in $CDCl_3$.

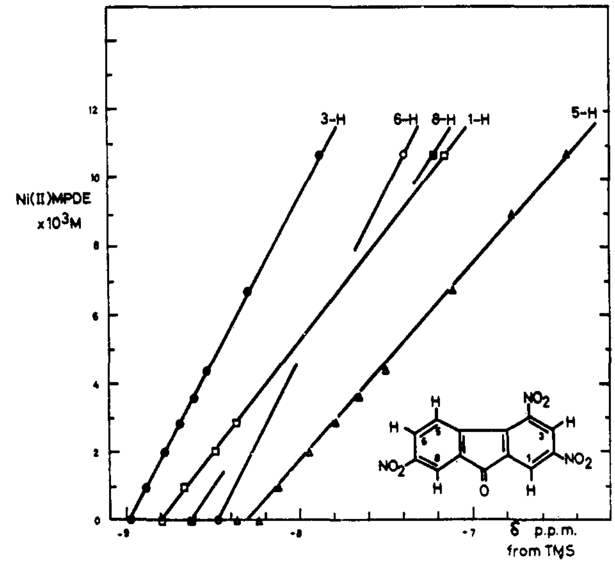

Figure 3. The dependences of the chemical shifts of the protons of I (0.03 *M*) on the concentration of $Ni^{II}MPDE$.

The shifts caused by $Co^{II}MPDE$ (Figure 2) are bigger, though now the peaks are broadened. The dependence on the $Co^{II}MPDE$ concentration is given in Figure 4 and the reciprocal gradients in Table II. The 8-H and 1-H peaks overlapped at high Co^{II}-MPDE concentrations. (Assigned resonances derived from $Co^{II}MPDE$ were not obtained in the TNF complex, but they have been located in another molecular complex[15] at higher $Co^{II}MPDE$ concentrations.) A

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[15] H. A. O. Hill, P. J. Sadler, and R. J. P. Williams, *J. Chem. Soc., Dalton Trans.*, in press.

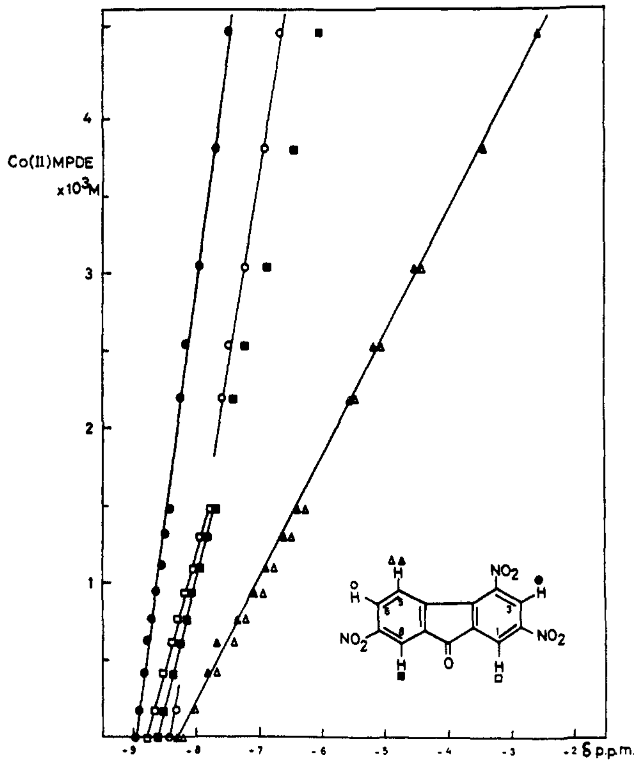

Figure 4. The dependences of the chemical shifts of the protons of I (0.03 *M*) on the concentration of Co^{II}MPDE.

Table II. 2,4,7-Trinitrofluorenone (0.03 *M*) Proton Shifts in the Presence of Cobalt(II) Mesoporphyrin IX Dimethyl Ester in CDCl$_3$ at 298 °K

	Reciprocal gradients (ppm mol^{-1} l. × 10^{-2})	Δ_1, ppm	K_1, l. mol^{-1}
1-H	7.25 ± 0.6	35.7 ± 4.6	172 ± 80
3-H	3.50 ± 0.3	17.3 ± 1.0	346 ± 129
5-H	12.7 ± 0.7	56.8 ± 1.4	470 ± 106
6-H	4.02 ± 0.4	20.7 ± 2.8	308 ± 157
8-H	6.05 ± 0.5	26.8 ± 1.1	377 ± 117

titration at constant Co^{II}MPDE concentration (9 × 10^{-4} *M*) was carried out to measure the formation constant and the shifts in the fully formed 1:1 complex. The results are given in Table II. We assume that these values of Δ_1 can be written where Δ_1(ring) are the shifts

$$\Delta_1 = \Delta_1(\text{ring}) + \Delta_1(\text{para})$$

due to the ring current, taken to be identical with those caused by Ni^{II}MPDE, and Δ_1(para) are additional shifts due to the single unpaired electron in Co^{II}MPDE. By subtraction we find the values of Δ_1(para) shown in Figure 5. As a check on the internal consistency of our data we note that ratios of these shifts with respect to 5-H are in reasonable agreement with those found (Table III) by the subtraction of the reciprocal gradients, Tables I and II.

We shall assume that the paramagnetic shifts of the TNF protons are metal-centered dipolar (pseudocontact) shifts.

Equations for dipolar shifts in a complex with C_{2v} symmetry have recently been described[16,17] in terms of the susceptibility components χ_x, χ_y, and χ_z, eq 2.

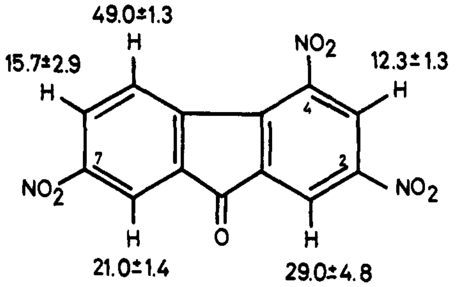

Figure 5. The paramagnetic shifts of the various protons of I.

Table III. Percentage Ratios of Paramagnetic Shifts

$\Delta_1(\quad)$para/ Δ_1(5-H)para	Fully formed shifts	Reciprocal gradients
5-H	100	100
1-H	59 ± 10	52 ± 9
8-H	43 ± 3	43 ± 5
6-H	32 ± 6	27 ± 4
3-H	25 ± 3	23 ± 3

$$\frac{\Delta H_{\mathrm{d}}}{H_0} = -\frac{1}{3r^3}[\chi_z - {}^1/_2(\chi_x + \chi_y)](3\cos^2\Omega - 1) + \frac{3}{2}(\chi_x - \chi_y)\sin^2\Omega\cos 2\theta \qquad (2)$$

Since no susceptibility data are available, we have investigated the g tensor anisotropy which, to first order, will provide information about the symmetry of the complex.

Complex formation between trinitrofluorenone and Co^{II}MPDE was clearly indicated by epr measurements as can be seen from Figures 6 and 7. The signals from Co^{II}MPDE itself were weak, and loss of intensity is probably caused by partial spin pairing through porphyrin dimerization. The signal at $g = 2$ and broad band to low field may be connected with this. Dimerization of metalloporphyrins has been detected by epr,[18] but the metal ion is not thought to play a major role in the association phenomenon.

The components of $g_\parallel$ and $g_\perp$ are more clearly resolved in the spectrum of the fully formed trinitrofluorenone complex, Figure 7. A spectral simulation including second-order and quadrupole interaction terms confirmed the interpretation in terms of axial symmetry. All the epr parameters are listed in Table IV.

In axial symmetry $\chi_z = \chi_\parallel$ and $\chi_x = \chi_y = \chi_\perp$ and, eq 2 becomes

$$\Delta H_{\mathrm{d}} H_0 = (\chi_\parallel - \chi_\perp)(3\cos^2\Omega - 1)/3r^3 \qquad (3)$$

$$= -D(3\cos^2\Omega - 1)/r^3 \qquad (4)$$

where Ω is the angle between the main symmetry axis of the complex and the direction vector from the metal atom to the nucleus whose resonance is being observed, and r is the metal-to-nucleus distance. Ratios with respect to a chosen standard proton are of the form

$$\Delta H_{\mathrm{d}}(i)/\Delta H_{\mathrm{d}}(0) = \langle(3\cos^2\Omega_i - 1)/r_i\rangle/\langle(3\cos^2\Omega_0 - 1)/r_0^3\rangle \qquad (5)$$

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[16] R. J. Kurland and B. R. McGarvey, *J. Magn. Resonance*, **2**, 286 (1970).

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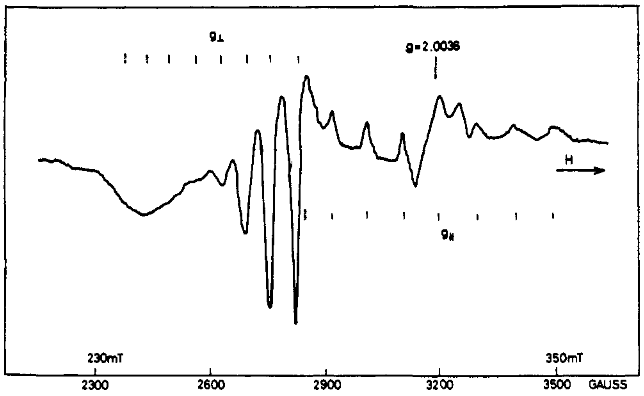

Figure 6. The epr spectrum of Co^{II}MPDE (10^{-2} *M*) in $CHCl_3$ at 133°K and 9145 MHz.

Table IV. Epr Parameters of Co^{II}MPDE and Its Complex with TNF

	Co^{II}MPDE estimated	Co^{II}MPDE·TNF estimated	Calcd[a]
$g_{\parallel}$	2.047	1.891	1.70
$g_{\perp}$	2.510	3.611	3.20
A, cm^{-1}	97×10^{-4}	179×10^{-4}	160×10^{-4}
(G)	(102)[b]	(203)[c]	(202)
B, cm^{-1}	81×10^{-4}	426×10^{-4}	380×10^{-4}
(G)	(69)[c]	(253)[d]	(254)

[a] The calculation assumed $Q = 4$ G and the half peak-to-peak width of the derivative of a single component line at a particular angle of 65 G. [b] Average six spacings. [c] Average four spacings. [d] Average seven spacings.

where the geometrical factors are to be averaged over all motions which are rapid on the nmr time scale. Since the protons being considered are all attached to a rigid aromatic fluorene framework, there are no intramolecular motions to be considered.

Given the ratios of Table III, is it possible to find a structure for this molecular complex with a metal position and symmetry axis orientation such that the angle and distance factors for each proton are consistent with eq 5?

The broadening of the resonance peaks also contains information about the structure of the complex. We can form similar ratios using the dipolar term of Sternlicht's equation (6).[19]

$$\frac{\delta\nu_{1/2}(i)}{\delta\nu_{1/2}(0)} = \frac{T_2^{-1}(i)}{T_2^{-1}(0)} = \frac{({}^1/_3(g_{\parallel}^2 + 5g_{\perp}^2) + (g_{\parallel}^2 - g_{\perp}^2)\cos^2\Omega_i)/r_i^6}{({}^1/_3(g_{\parallel}^2 + 5g_{\perp}^2) + (g_{\parallel}^2 - g_{\perp}^2)\cos^2\Omega_0)/r_0^6} \quad (6)$$

Estimates of the broadening ratios were obtained at 60 MHz by subtracting the diamagnetic line widths of the TNF multiplets from those in the presence of Co^{II}MPDE. This indicated that 5-H was about three times as broad as 3-H and broader than the other peaks. For the purposes of computation, *vide infra*, we have taken the ratios of spin–spin relaxation times with respect to 5-H to lie within the range 60 ± 45. With $g_{\parallel} = 1.89$ and $g_{\perp} = 3.61$ the broadening function becomes $(22.9 - 9.5\cos^2\Omega)/r^6$.

In order to calculate shift and broadening ratios and compare them with those observed, we have to measure Ω and r for the TNF protons for each metal position and symmetry axis orientation considered. We have developed a computer procedure to do this.

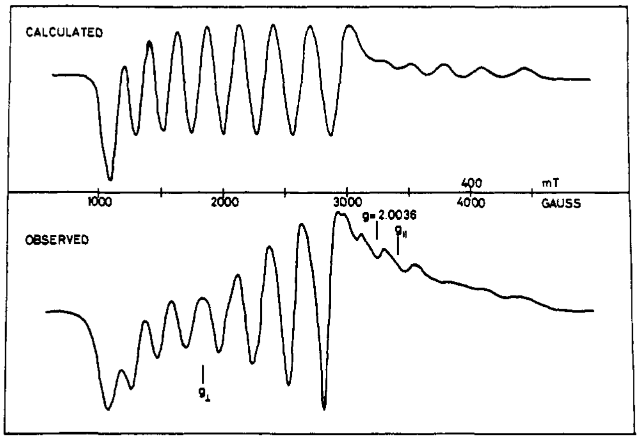

Figure 7. The epr spectrum of Co^{II}MPDE (10^{-2} *M*) in the presence of I (3×10^{-2} *M*) in $CHCl_3$ at 133°K and 1968 MHz.

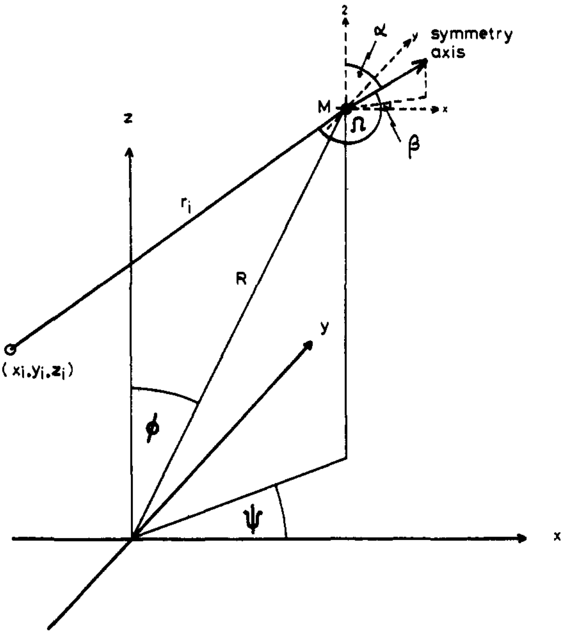

Figure 8. Coordinate axes for protons, metal, and symmetry axis.

Computation. The program places the trinitrofluorenone molecule in a fixed Cartesian coordinate frame of reference and the metal position is defined with spherical polar coordinates (R, φ, ψ) as shown in Figure 8. Two angles (α, β) are sufficient to define the orientation of the unit vector representing the metal symmetry axis. The porphyrin ring lies approximately in a plane perpendicular to this axis. Vectorial algebra gives the expressions for r_i and Ω_i.

$$r_i = [(R\sin\varphi\cos\psi - x_i) + (R\sin\varphi\sin\psi - y_i)^2 + (R\cos\varphi - z_i)]^{1/2} \quad (7)$$

$$\cos\Omega_i = [(R\sin\varphi\cos\psi - x_i)(\sin\alpha\cos\beta) + (R\sin\varphi\sin\psi - y_i)(\sin\alpha\sin\beta) + (R\cos\varphi - z_i)(\cos\alpha)]/r_i \quad (8)$$

The scan to search for ratios consistent with experimental observations involved computations at metal

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(19) H. Sternlicht, *J. Chem. Phys.*, **42**, 2250 (1965).

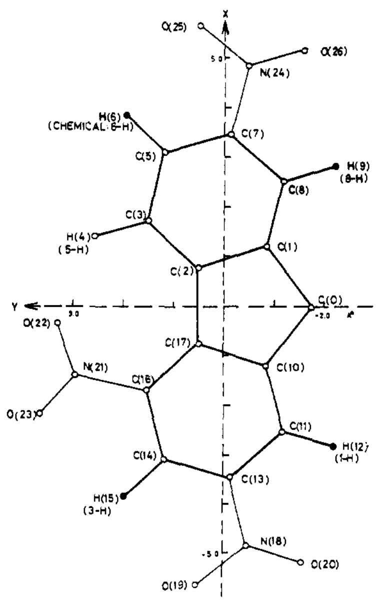

Figure 9. 2,4,7-Trinitrofluorenone coordinates.

positions on the surface of a sphere of radius R. At each position the metal vector could also be scanned over the surface of a sphere. Initial, final, and incremental values of R, φ, ψ, α, and β were specified in the input, and the program operated with a set of five loops. At fixed values of R, ψ, and α, β was successively incremented until the required range had been covered. The value of α was then incremented and the inner loop repeated and so on for ψ, φ, and R. The range of acceptable percentage ratios was also specified, and the output consisted of R, φ, ψ, α, and β, the direction cosines of the metal vector, the calculated shift and broadening functions, and their percentage ratios. The program did not exclude solutions with short van der Waal's contacts. There were four main stages to the calculation. (i) The coordinates of the fluorene skeleton (Figure 9) were taken from the reported crystal structure of 9-dicyano-2,4,7-trinitrofluorenone,[20] and a C–H bond length of 1.1 Å, directed along the angle bisector, was assumed. (ii) The computer installation enabled a three-dimensional outline of the molecule to be displaced on a cathode ray tube screen, the approximately planar fluorene skeleton was rotated into the xy plane, and the origin was centered at the intersection of the diagonals of the five-membered ring. (iii) The first scan, for ratios of shifts within the range given in Table III under the heading "computation," was at R = 5 Å with χ = 5–85°, ψ = 5–355°, α = 5–85°, and β = 5–355°, with a 10° increment on all angles. The metal, M, and axis orientation were scanned over hemispheres since symmetry considerations show that with approximately planar molecules there will be two identical sets of angles and distances with the metal above or below TNF and the axis pointing toward or away from it. The 105 conformations required about 60 min of Argus computing time and there were two acceptable solutions: R = 5.0 (25, 105, 25, 105), M (−0.55, 2.04, 4.53); R = 5.0 (25, 115, 25, 115); M (−0.89, 1.92, 4.53). They are written in the form R = 5.0 (φ, ψ, α, β), M (x, y, z). A similar scan at R = 4 Å produced nine solutions: R = 4.0 (5, 195, 5, 215, 225, 235), M (−0.34, −0.09, 3.98); R = 4.0 (5, 205, 5, 225, 235), M (−0.32, −0.15, 3.98); R = 4.0 (5, 215, 5, 235), M (−0.29, −0.20, 3.98); R = 4.0 (5, 225, 5, 245), M (−0.25, −0.25, 3.98); R = 4.0 (5, 235, 5, 255), M (−0.20, −0.29, −3.98); R = 4.0 (15, 225, 15, 235), M (−0.73, −0.73, 3.86). The calculated values of $(3\cos^2\Omega - 1)/r^3$ were all positive. This agrees with eq 4, since $g_{\parallel} - g_{\perp}$ is negative ($\chi_{\parallel} - \chi_{\perp}$ is also negative for cobalt(II) phthalocyanine[21]) and high field shifts are predicted, as observed. In subsequent scans the broadening ratios were also calculated. (iv) The broadening function $(22.9 - 9.5\cos^2\Omega)/r^6$ was used, although ratios <100% differed from those of an r^{-6} function by <15%. The computer gave percentage broadening ratios within 999% of those required, and the results were filtered by inspection to find shift acceptable solutions for which the broadening ratios were also acceptable. The limits and increments of all scans had to be carefully chosen both to suit the amount of computer time available and to track all solutions.

The results can be summarized. (1) No solutions were found at R = 3.5 Å. The shift acceptable solutions at R = 3.7 Å were rejected since they required 1-H to be more than twice as broad as 5-H. The broadening function is very sensitive to small changes in metal position at these distances. (2) There were shift and broadening solutions at R = 3.9 Å. The TNF and porphyrin planes were parallel (Figures 10 and 11) as indicated by α, the "angle of tilt," 1–5°, with the metal situated above the origin. (3) As R increased the metal moved away from the origin in the positive y direction to find solutions, *i.e.*, along the symmetry axis of TNF away from the carbonyl group. The acceptable angle between the planes increased from 1° at 3.9 Å to 21° at 4.9 Å (Figures 10 and 11). Effectively, 3-H and 5-H remained fixed relative to the metal and its axis, while the angle between the planes increased. All solutions beyond R = 5.1 Å required that 3-H be too broad and 8-H not broad enough compared to 5-H and could be rejected. (4) In general, the broadening filter excluded higher angles of tilt for a given set of shift acceptable solutions. For example, at R = 3.9 Å acceptable tilts were reduced from 1–13° to 1–5°, and at R = 4.9 Å from 17–35° to 17–25° when the broadening filter was included.

The uncertainties in the parameters for calculated shift and broadening solutions can be illustrated: at R = 3.9 Å φ = 4 ± 4°, ψ = 175 ± 30°, α = 4 ± 4°, β = 225 ± 20°; and R = 4.9 Å ψ = 21 ± 4°, ψ = 115 ± 10°, α = 20 ± 5°, β = 115 ± 15°.

Discussion

The results show that the association of $\mathrm{Co^{II}MPDE}$ which takes place in $\mathrm{CDCl_3}$, is broken up by the addition of I with the concomitant formation of a 1:1 complex, confirming earlier spectroscopic investigations.

It is obvious that both $\mathrm{Ni^{II}MPDE}$ and $\mathrm{Co^{II}MPDE}$ act as shift reagents. The main assumptions used in attempting to derive detailed geometric information from the $\mathrm{Co^{II}MPDE}$ shift data are: (1) that the shift

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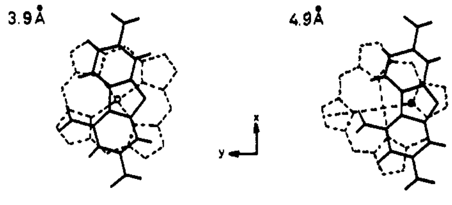
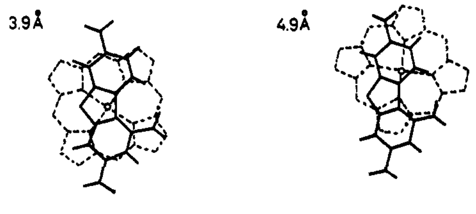
(21) R. L. Martin and S. Mitra, *Chem. Phys. Lett.*, 3, 183 (1969).



A. Projection down z axis



B. Projection along metal axis

Figure 10. Structures of the Co^{II}MPDE–I complex. In A, I is in the reference frame drawn in Figure 9 and the metal has a positive z coordinate. The metal symmetry axis is a dotted line. For completeness, the porphyrin surrounding the metal has been outlined using the atom positions given by E. B. Fleischer, *J. Amer. Chem. Soc.*, 85, 146 (1963). It is slightly concave and its orientation is arbitrary. B is a view along the metal symmetry axis from beneath I. The prophyrin lies in an arbitrary orientation in the xy plane.

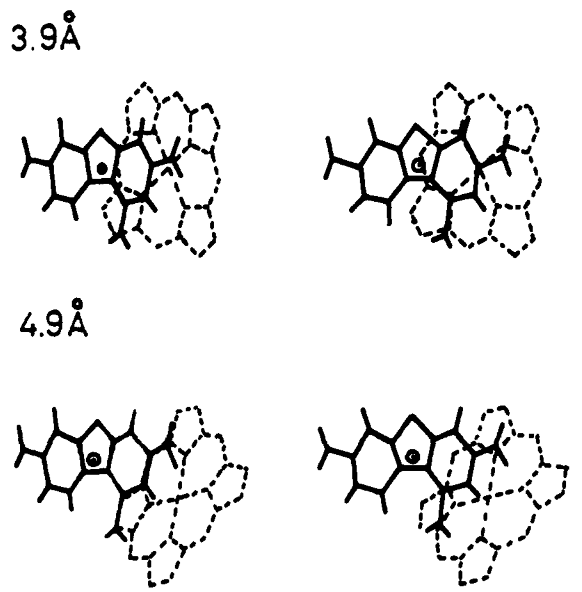


Figure 11. Stereo view of Co^{II}MPDE–I complex. The correct viewing distance for the stereo pairs is 30 cm.

is caused by the dipolar term; (2) that if (1) is justified, the g (or χ) parameters are tetragonal and hence eq 3 is applicable; (3) that the diamagnetic contribution can be reliably accounted for using the data derived from the Ni^{II}MPDE shifts. Though the reasonableness of the derived structures suggests that these assumptions are justified, we would add that in every case examined[9–11] we have found that the shifts of the non-porphyrin component of the molecular complex move to high field as expected if $g_\perp > g_\parallel$. In no case did we find alternation in Δ_1(para) which might result from direct electron (spin) transfer; in other words the contact contribution appears to be negligible. This may have the corollary that the charge transfer contribution to the ground state of molecular complexes contributes little to their stabilization. That the dipolar approximation, which assumes a point dipole for electron (and proton) may be an inadequate representation of the single unpaired electron in the ^{2}A ground state of Co^{II}MPDE is always possible, but no reasonable and practicable alternative is at hand. Moreover, we were able to confirm[15] that the paramagnetic shifts of the Co^{II}MPDE protons themselves are all to low field and in accordance with the predictions of the dipolar term.

In all the complexes of Co^{II}MPDE examined so far $g_\perp > g_\parallel$ with little evidence for a significant rhombic distortion. Consequently we believe the ratio method to be justified. The use of Ni^{II}MPDE as a diamagnetic blank which includes the ring current contribution implies that the structures of the complexes are closely related. While we have no conclusive evidence of this, both in the complexes of I and most others examined the qualitative structures which can be inferred from the Ni^{II}MPDE shift data are also consistent with those calculated for the Co^{II}MPDE complexes. Thus in this case all the protons of I might be expected to lie within the porphyrin ring and therefore should be shifted to high field, as is observed.

The "structures" (Figures 10 and 11) of the complex which are found to be compatible with the shift data and consistent with the broadening data are reasonable in terms of the known structures of molecular complexes in the crystalline state. However the concept of "structure in solution" is, itself, a difficult one, due to the presence of solvent and the rapid thermal motion of all components. The methods of investigation described in this paper indicate probably the dominant "correlations of orientation" which are thought[22] to be an important part of the structure of all molecular liquids. Thus one need not expect a unique structure to emerge from these and similar investigations. The family of structures with $R = 4.0 \pm 0.2$ Å are closely related to those determined for similar complexes in the crystalline state in that the planes of the Co^{II}MPDE and I are parallel. The interaction of I with the porphyrin is probably with the macrocycle and not with the metal and the relative orientation probably mazimizes van der Waal's interactions. The method of investigation described herein would not detect buckling of the porphyrin nor indeed movement of the cobalt out of the porphyrin plane. However in spite of these limitations it is felt that the results do suggest that it is possible to use Co^{II}MPDE in such a way as to reveal detailed geometric information about the "structures" of molecular complexes in solution.

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(22) P. A. Egelstaff and D. I. Page, *Mol. Phys.*, 20, 881 (1971).