Solvent and Substituent Effects on the
Spin Resonance Spectra of Metalloporphyrins[1a]

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The effect of varying the solvent and the peripheral sub-
stituents on the spin resonance spectra of copper and
silver porphyrins and of copper chlorins has been in-
vestigated in dilute solutions at low temperatures. Solute
dimerization predominates at 10^{-3} to 10^{-4} M concentra-
tions, from $77°K$. almost to room temperature, in
solvents such as benzene and chloroform. Dimerization
is partially impeded if large groups, such as cholesteryls,
are attached to the porphin by esterification. In ace-
tone and particularly in 1-chloro- and 1-bromonaph-
thalenes, dimerization does not occur except in compounds
with very strongly electron-withdrawing substituents or
exocyclic rings. The chlorin structure inhibits solute
aggregation. The formation of pyridinate complexes is
reflected in a marked increase in the g factor and by a
decrease in the nitrogen hyperfine splitting parameter.
In the case of compounds with maximum associative
tendency, or where the metal–base link is weak (e.g.,
the silver complexes), pyridine solution does not preclude
dimerization at low temperatures through π–π bonding
between porphyrin molecules. The four nitrogens remain
equivalent throughout the range studied, from tetraphenyl-
porphin and etioporphyrin to pyropheophorbide a and
chlorin e-6.

Introduction

The metal-to-nitrogen bonding parameters of copper
and silver porphyrins and phthalocyanines can be
determined by electron spin resonance spectroscopy of
their dilute and frozen solutions. The theory and
experimental observations for a few of these compounds
have been reported and discussed from this laboratory
in previous communications.[2] In particular, the inter-
action between the odd electron of the paramagnetic
metal and the pyrrole nitrogens can be deduced from
the spacing of the nitrogen hyperfine lines and the
variations in the g factor, from which the σ-covalency of
these bonds can be calculated, since it is proportional
to the anisotropic hyperfine constant. The calculated
extent of π-bonding varies with the particular scheme
that is assumed for the arrangement of the molecular
orbitals and cannot be resolved unambiguously from
the equations of Abragam and Pryce.[3]

The solvents, the peripheral substituents on the
porphyrin ring, and the temperature modify the spin
resonance spectra of copper and silver porphyrins.
These variations may concern the g factors, the nitrogen
hyperfine splittings, and, in some instances, the gross
appearance of the spectra. They are interpreted as
evidence for the different states of solvation and solute
aggregation that occur in these systems.

Experimental

The spin resonance spectra were taken on an X-band
Varian Model V 4500 spectrometer, utilizing 100-kc.
modulation, and generally at $77°K$. The solutions used
varied from 10^{-4} to 10^{-3} M. The spectra were calibrated
against polycrystalline diphenylpicrylhydrazyl (for
which g_0 is accurately known to be 2.0036) and com-
puted by the method of Roberts.[3b,4] Hyperfine
broadening due to solute–solute interactions becomes
noticeable for all of the compounds at concentrations
exceeding 5×10^{-2} M. At lower molarities, the
appearance and parameters of the spectra are, in
general, independent of concentration within the limits
mentioned. Solutions under 10^{-4} M in the metallo-
porphyrin were found to be too dilute for proper resolu-
tion of the spectra.

The cupric and argentic complexes of these com-
pounds were formed in each case by heating the free
bases,[5] dissolved in pyridine or in acetic acid, with an
excess of cupric or argentous acetate. The resulting
metal derivatives were separated by chromatography
and recrystallized from benzene–methanol or chloro-
form–methanol. The metal-free bases used were
highly purified compounds for which the observed and
calculated analyses are in excellent agreement. The
electronic spectra of the metallic complexes coincide
with those given in the literature, and, in a number of
cases, their elemental analyses were also obtained as a
further confirmation of purity and found to be satis-
factory. The e.s.r. samples were prepared by dissolu-
tion of the complexes in reagent grade solvents (used
without further treatment) in the atmosphere and at
room temperature. No attempts were made to exclude
oxygen from the quartz sample tubes. The structures of
the porphyrins studied are given in Table I.

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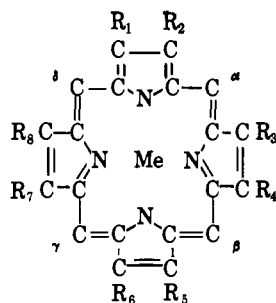(4) E. M. Roberts, Dissertation, The Johns Hopkins University,
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J. Org. Chem., 8, 205 (1943); (j) P. E. Wei, Dissertation, The Johns
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Table I. Structures of Metalloporphyrins

Compound[a]	R₁	R₂	R₃	R₄	R₅	R₆	R₇	R₈	α	β	γ	δ
Mesoporphyrin IX dimethyl ester (a)	M	E	M	E	M	PrM	PrM	M	H	H	H	H
Deuterioporphyrin IX dimethyl ester (a)	M	H	M	H	M	PrM	PrM	M	H	H	H	H
Diacetyldeuterioporphyrin IX dimethyl ester (a)	M	A	M	A	M	PrM	PrM	M	H	H	H	H
Dinitrodeuterioporphyrin IX dimethyl ester (b)	M	NO₂	M	NO₂	M	PrM	PrM	M	H	H	H	H
Protoporphyrin IX (c)	M	V	M	V	M	PrH	PrH	M	H	H	H	H
Etioporphyrin II (f)	M	E	E	M	M	E	E	M	H	H	H	H
Desoxophylloerythrin monomethyl ester (g)	M	E	M	E	M	CH₂CH₂	PrM	M	H	H		H
Desoxophylloerythroetioporphyrin (g)	M	E	M	E	M	CH₂CH₂	E	M	H	H		H
Pyrroporphyrin XV monomethyl ester (d)	M	E	M	E	M	H	PrM	M	H	H	H	H
Phylloporphyrin XV monomethyl ester (e)	M	E	M	E	M	H	PrM	M	M	H	H	H
Mesoporphyrin IX dicholesteryl ester (h)	M	E	M	E	M	PrCh	PrCh	M	H	H	H	H
Tetraphenylporphin (i)	H	H	H	H	H	H	H	H	Ph	Ph	Ph	Ph
Pyropheophorbide a monomethyl ester (j)	M	V	M	E	M	O ‖ C—CH₂	PrM, H	M, H	H	H		H
Chlorin e-6 trimethyl ester (j)	M	V	M	E	M	FM	PrM, H	M, H	H	H	PrM	H

[a] Letters in parentheses after the compound name refer to the reference subdivisions in reference 5. [b] M = CH₃, E = CH₂CH₃, V = CH=CH₂, PrH = CH₂CH₂COOH, PrM = CH₂CH₂COOCH₃, FM = COOCH₃, Ph = C₆H₅, A = COCH₃, PrCh = CH₂CH₂COOC₂₇H₄₅, Me = Cu or Ag.

Results

According to the solvent employed, three types of spectra are recorded for 0.001 M copper and silver porphyrins at low temperatures. Under equivalent conditions of optimum resolution on our instrument, these types are shown in Figures 1, 2, and 3. In
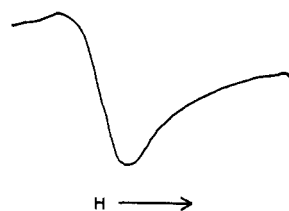

Figure 1. E.s.r. spectrum of 0.001 M silver deuterioporphyrin IX dimethyl ester in benzene at −44°.

benzene and in chloroform the hyperfine structure is in general obliterated, and only a single broad signal can be observed (Figure 1). For almost all of the compounds studied, the perpendicular (high magnetic field) side to the hyperfine spectrum is well resolved in 1-chloro-

and in 1-bromonaphthalene, as shown in Figure 3. (The low-field side is always resolved imperfectly, because of the smaller number of molecules which are
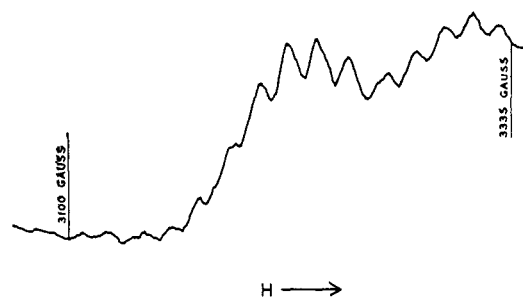

Figure 2. High-field side, e.s.r. spectrum of 0.001 M copper chlorin e-6 trimethyl ester in 1-chloronaphthalene at 77°K.

oriented parallel to the molecular axis in a random distribution of the solute in a glass.[6])

In the case of silver compounds in pyridine, and of copper compounds with certain highly electronegative

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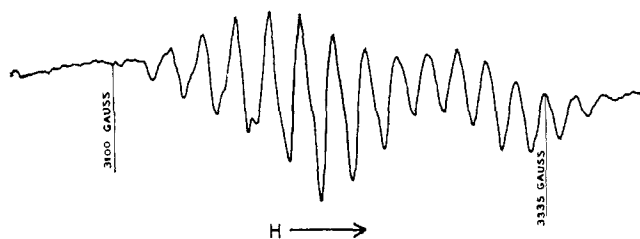
Figure 3. High-field side, e.s.r. spectrum of 0.001 M copper mesoporphyrin IX dimethyl ester in 1-chloronaphthalene at 77°K.
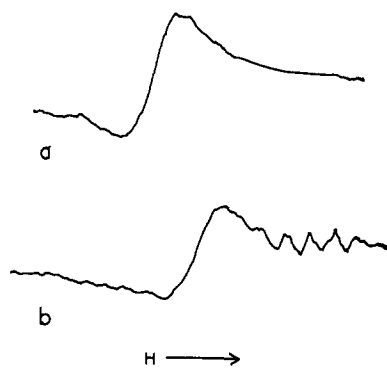

Figure 4. E.s.r. spectrum of 0.001 M copper deuterioporphyrin IX dimethyl ester in benzene: (a) at $-1°$, (b) at $0°$.

groups or exocyclic rings attached directly to the periphery of the pyrroles, an intermediate case (Figure 2) is observed, where there is some indication of the hyperfine structure. This structure is regained if a small quantity (approximately 0.001 M) of the metal-free compound is added to the solution. In all cases, the hyperfine structure can be resolved at room temperature. The transition temperature between the broadened signals of the first type and the incipient hyperfine structure of Figure 2 depends upon the metal, the solvent, and the peripheral substituents. With silver deuterioporphyrin IX dimethyl ester in chloroform, the transition occurs at $-45°$, but in benzene the broadened signal persists, as the temperature is raised, until $-6°$. In the case of the copper compound of this porphyrin in benzene, incipient hyperfine structure is observed only beyond $0°$ (Figure 4).

The disappearance of the structure occurs for a variety of solvents besides chloroform and benzene; it is also observed for 1,4-dioxane, 1,2-dichloroethane, bromobenzene, nitrobenzene, and carbon tetrachloride. Spectra in 1-fluoronaphthalene solution differ from those in 1-chloro- or in 1-bromonaphthalene; the hyperfine is obliterated in the fluorine derivative for the copper compounds, and for the silver complexes it is well resolved only in very dilute solution (approximately 2×10^{-4} M; see Figure 5).

With solvents for which the hyperfine structure is resolved, so that differences in the g factor and in the hyperfine splittings can be measured accurately, it was found that these parameters were sensitive to the solvent and, to a smaller degree, to the effect of the pyrrole and bridge substituents. The patterns of such spectra, however, remained essentially constant over a very wide range of peripheral substituents; the equality of the four nitrogens, an obvious feature in the spectrum

of copper etioporphyrin II,[3b] is retained in all of the compounds, including copper pyropheophorbide a and copper chlorin e-6.

A series of different porphins was examined in acetone, 1-chloronaphthalene, and pyridine. The latter were chosen as representative of the various solvents in which the hyperfine lines are resolved for most of the copper compounds. The heavier fatty acids, esters, benzyl alcohol, benzaldehyde, and ethyl iodide belong to this class of porphin solvents. A wide variety of the complexes were found soluble in the three media chosen to the required extent of at least 5×10^{-4} M.
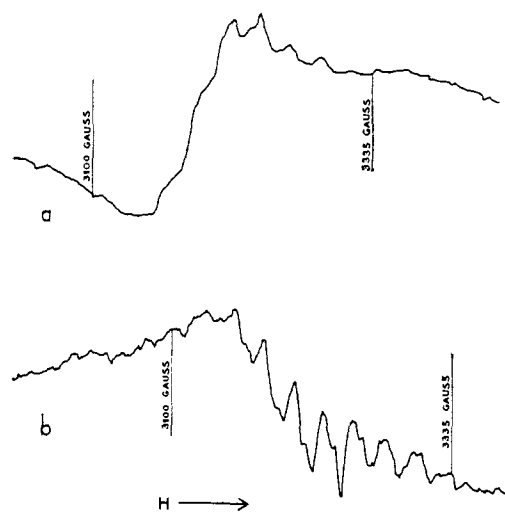

Figure 5. E.s.r. spectrum of silver deuterioporphyrin IX dimethyl ester in 1-fluoronaphthalene at 77°K.: (a) 0.0015 M, (b) 0.0002 M.

With pyridine, for which optical studies had previously shown the formation of pyridinate complexes by association of the solvent with the metal in the porphyrin,[7,8] there was a pronounced translation of $g_\perp$ toward higher values, as well as a lowering in the nitrogen hyperfine splitting. In the silver complexes, however, where the optical results[9] had indicated much weaker bonding of pyridine to the metal, the hyperfine structure could not be clearly resolved. (Even in piperidine at room temperature, in contrast with the behavior of copper porphyrins,[10] the near-ultraviolet Soret peak in the silver compounds remains unsplit. In going from acetic acid to pyridine, the Soret absorption maximum is shifted by only 3 mμ from 404 to 407 mμ for silver deuterioporphyrin IX dimethyl ester, but by 6 mμ from 392 to 398 mμ for the corresponding ester of copper mesoporphyrin IX.)

The perpendicular nitrogen hyperfine splitting was found to be, in general, a function of the solvent alone. Undoubtedly more accurate determinations would show that there is also a substituent effect in this parameter, corresponding to the variations in $g_\perp$; how-

(7) W. S. Caughey, R. M. Deal, B. D. McLees, and J. O. Alben, J. Am. Chem. Soc., 84, 1735 (1962).
(8) E. W. Baker, M. S. Brookhart, and A. H. Corwin, ibid., 86, 4587 (1964).
(9) J. R. Miller and G. D. Dorough, ibid., 74, 3977 (1952).
(10) A. H. Corwin, D. G. Whitten, E. W. Baker, and G. G. Kleinspehn, ibid., 85, 3621 (1963).

ever, the precision of our spectra does not, in general, allow for such small differences in the nitrogen hyperfine to be observed. For the copper compounds this parameter is 16.6 gauss in acetone, 16.0 in 1-chloronaphthalene, and 15.4 in pyridine (± 0.2 gauss). The dinitrodeuterioporphyrin compound, however, shows 15.4 and 14.3 gauss for 1-chloronaphthalene and pyridine, respectively. For the more covalent silver compounds, the perpendicular nitrogen hyperfine is approximately 24.5 gauss in 1-chloronaphthalene and varies slightly with solvent.

Both the copper and silver derivatives of meso-porphyrin, deuterioporphyrin, and diacetyldeuterioporphyrin IX dimethyl esters were examined at 77°K. in 0.001 M solutions. For the silver complexes, the hyperfine structure is almost obliterated in pyridine. For the copper porphyrins, the meso- and deuterio-spectra were practically identical with each other both in pyridine and in acetone, with $g_\perp$ at 2.0753 and 2.0756, and at 2.0264 and 2.0621, respectively, for the two complexes and solvents. The hyperfine structure of silver diacetyldeuterioporphyrin could not be resolved
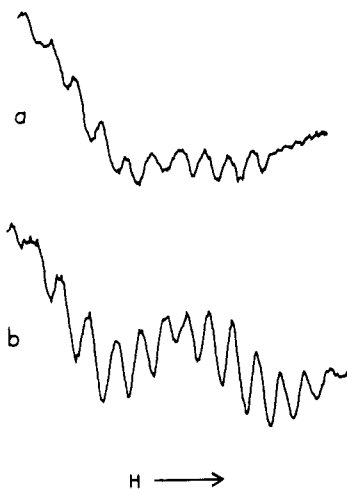

Figure 6. High-field side, e.s.r. spectrum of 0.001 M copper desoxophylloerythrin monomethyl ester in pyridine at 77°K.: (a) with no free base, (b) 0.001 M in metal-free desoxophylloerythrin monomethyl ester.

in any solvent; for the corresponding copper compound, it was broadened out in acetone and to a smaller degree in pyridine, where $g_\perp$ was at 2.0762, a very slight increase over the deuterioporphyrin value. In 1-chloronaphthalene, however, the three copper complexes showed significant changes in the $g_\perp$ factor, which increased with increasing electron-withdrawing character of the side groups: 2.0646, 2.0657, and 2.0668 for mesoporphyrin, deuterioporphyrin, and diacetyldeuterioporphyrin, respectively. The solvent effect for the silver complexes was of the same magnitude; $g_\perp$ changed from 2.0294 in acetone to 2.0320 in chloronaphthalene, in the case of deuterioporphyrin.

Copper dinitrodeuterioporphyrin IX dimethyl ester exhibited the highest $g_\perp$ factor as well as the smallest hyperfine splittings in the copper series. The hyperfine structure was clear in 1-chloronaphthalene, but was broadened out in pyridine. The hyperfine could be

restored in pyridine by addition of an equal amount of the free base.

The much smaller solubility of the unesterified metalloporphyrins in organic media limited the examination of copper protoporphyrin IX to a basic solvent, pyridine. In it a slight increase of $g_\perp$ from the case of the meso- and deuterioporphyrin esters was observed, from 2.0756 to 2.0761.
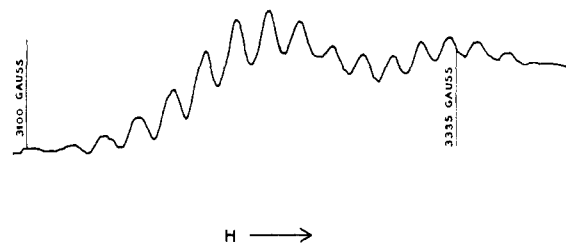

Figure 7. High-field side, e.s.r. spectrum of 0.001 M copper mesoporphyrin IX dicholesteryl ester in chloroform at 77°K.

Etioporphyrin II and desoxophylloerythroetioporphyrin differ significantly only in that the latter has an exocyclic ring adjacent to the third pyrrole group, as in the case of the chlorophylls. The differences between the spin resonance spectra of their copper complexes, however, are very marked. Copper etioporphyrin itself does not differ appreciably in this respect from mesoporphyrin IX dimethyl ester, either in pyridine or in 1-chloronaphthalene. In copper desoxophylloerythroetioporphyrin, while the $g_\perp$ factor remains the same as for etioporphyrin, the hyperfine structure is greatly broadened out at equivalent concentrations (Figure 6). This loss of the hyperfine structure is greatest for pyridine and smallest for 1-chloronaphthalene, and although concentration dependent, it is observed to a marked degree throughout the range available for the spin resonance studies. The further change in going from desoxophylloerythroetioporphyrin to desoxophylloerythrin monomethyl ester has no apparent effect. The addition of the metal-free base (0.0005–0.001 M) restores the hyperfine structure but further additions are not significant.

Pyrroporphyrin and phylloporphyrin XV monomethyl esters differ only in that phylloporphyrin has a methyl group on the α-bridge position. As was expected from the nature of its side groups, copper pyrroporphyrin shows a $g_\perp$ factor close to that of mesoporphyrin: 2.0746 and 2.0753, respectively, in pyridine, and 2.0643, 2.0646 in 1-chloronaphthalene. However, phylloporphyrin shows a considerably higher $g_\perp$ factor in the three solvents.

Of all the complexes examined, only in the highly soluble compound, copper mesoporphyrin IX dicholesteryl ester, was the hyperfine structure fairly well resolved for copper compounds in chloroform at 77°K. (Figure 7) and, at least partially, in benzene. The $g_\perp$ values in both cases were the same as those for the dimethyl ester of mesoporphyrin in acetone.

In copper tetraphenylporphin no appreciable deviations from the other porphyrins, despite the absence of bridge hydrogens, were detected. The only anomaly in this case was that in 1-chloronaphthalene $g_\perp$ was close

to the value for deuterioporphyrin, while in pyridine the two compounds gave very different parameters (2.0756 for deuterioporphyrin, 2.0776 for tetraphenyl-porphin). This may be explained by the fact that the ligand in the copper tetraphenylporphin–pyridine complex is more tightly bound than in the copper deuterio-porphyrin complex owing to the electron-withdrawing effect of the four phenyl rings.

Pyropheophorbide *a*, like desoxophylloerythrin, has an exocyclic ring; chlorin e-6, as in the case of diacetyl-deuterioporphyrin, has a strongly electron-withdrawing group attached directly to the macrocycle. Pyropheo-phorbide *a* exhibits a well-defined hyperfine in both pyridine and 1-chloronaphthalene, but not in acetone. As with diacetyldeuterioporphyrin, the hyperfine struc-ture is poorly resolved in both of the former solvents for chlorin e-6, and disappears completely for acetone. The $g_\perp$ for pyropheophorbide *a* in 1-chloronaphthalene is comparable to the value for deuterioporphyrin, but exceeds it in pyridine; chlorin e-6 exhibits the highest $g_\perp$ of all the copper complexes examined, except for dinitrodeuterioporphyrin.

Discussion

With nonpolar solvents at the temperature of liquid nitrogen, the disappearance of the hyperfine structure can be explained by assuming that even at the low concentrations used, the porphyrins and chlorins exist essentially in the form of loose solute aggregates. The superposition of the field of the neighboring molecules on the external magnetic field leads to a spread of resonance frequencies within each quantum level of the paramagnetic system. This results in the phenomenon of spin–spin dipolar broadening of the spectral lines.

Association at concentration levels between 10^{-4} and 10^{-3} M has a strong effect on the spin resonance spectra almost to room temperature and is remarkably sensitive to the solvent. The weakly hydrogen-bonding property of chloroform results in significantly less association at the same temperature than is the case for benzene. Acetone, a hydrogen-bonding solvent, with which the metal interaction must at best be very slight (since the $g_\perp$ factor for its solutions is substantially that found for chloroform or benzene), gives complete dissociation for the greater part of the complexes studied. When very bulky side groups are introduced, such as cholesteryls, the porphin macrocycles are kept apart and aggregation is for the most part prevented. (The influence of phytyl chains on the association equilibrium of pheophytins could not be determined from nuclear magnetic resonance experiments.[11]) Sol-ubilities at room temperature, however, cannot be simply correlated to the degree of association. Solute–solute interactions, for example, are found to be strong in chloroform and pyridine, which are generally very good solvents for these complexes, but are weak in poorer solvents such as acetone or benzyl alcohol. For the same medium, higher solubilities are com-monly exhibited by those compounds which do not collapse the e.s.r. hyperfine structure.

With molecules such as 1-chloro- and 1-bromonaph-thalene, the strong interaction between the extensive

π-systems of solvent and solute results in complete dissociation of the dimers in most cases. When fluorine replaces chlorine in the solvent molecule, the perturbation in the resonating system of naphthalene is such that solute association again occurs except at very low concentrations. The effect of 1-chloronaphthalene is shown in the optical spectrum by a shift of approxi-mately 10 mμ toward the red in the near-ultraviolet maxima (with respect to the values in acetone) in both metal-free porphyrins and metalloporphyrins. This shift is of about 7 mμ in the visible maxima, but in the case of 1-fluoronaphthalene, the displacements are only of 7 and 5 mμ, respectively.

With the π-bonding solvent, chloronaphthalene, there is a regular and appreciable increase in the $g_\perp$ as the peripheral substituents become more electron with-drawing, from mesoporphyrin IX dimethyl ester to dinitrodeuterioporphyrin dimethyl ester, an increase which correlates well with the σ-constants for the side groups.[12] Baker[5g,8] has observed a similar correlation for the stability constants of substituted nickel deuterio-porphyrin dimethyl ester–piperidine complexes. The correlation of the $g_\perp$ values with a linear free energy parameter indicates a correspondence between the spin–orbit coupling and the bond energy, *i.e.*, the covalent character. In pyridine no such regular variation in $g_\perp$ is observed. In this solvent the $g_\perp$ is being affected directly by both the ring substituents and the complexed pyridine ligand.

In pyridine solution the effect of complex formation is clearly shown by the withdrawal of electron density at the nitrogens, as mentioned previously. In some instances there is an apparent reversion to the type of spectrum met with in noninteracting solvents. Even for those compounds where the spectrum is of this latter type, $g_\perp$ retains a value characteristic of pyridine solvation. This, in particular, is the case for (a) porphyrins with exocyclic rings, such as desoxophyl-loerythrin, for which $g_\perp$ corresponds to that of the similarly substituted etioporphyrin; and (b) chlorins and porphyrins without exocyclic rings but with strongly electron-withdrawing groups, for which high values of $g_\perp$ are found.

Aggregation would not be expected to occur in pyridine, yet the disappearance of the hyperfine struc-ture cannot be explained by the increasing loss of square-planar symmetry[13] as pyridine molecules be-come more closely bound to the metal with increasing peripheral electronegativity,[7] since the $g_\perp$ factors are independent of the broadening effect in the hyperfine structure.

The formation of two types of aggregates in chloro-phyll compounds has recently been examined by molecular weight and nuclear magnetic resonance studies[11,14] on solutions in the range between 0.06 and 0.2 M.[15] In nonpolar solvents, the magnesium-

(11) G. L. Closs, J. J. Katz, F. C. Pennington, M. R. Thomas, and H. H. Strain, *J. Am. Chem. Soc.*, **85**, 3809 (1963).

(12) J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 90.

(13) B. R. McGarvey, *J. Phys. Chem.*, **61**, 1232 (1957).

(14) J. J. Katz, G. L. Closs, F. C. Pennington, M. R. Thomas, and H. H. Strain, *J. Am. Chem. Soc.*, **85**, 3801 (1963).

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free derivatives form weakly bonded aggregates, probably because of $\pi-\pi$ interactions, but the magnesium-containing compounds dimerize more strongly in such media, through metal links to ketone or aldehyde oxygens of neighboring molecules. Recent magnetic resonance work[16] on magnesium etioporphyrin II and magnesium tetraphenylporphin has confirmed that this latter type of dimerization does not occur in the absence of polar side groups on the porphin. The aggregation met with in our spin resonance experiments is enhanced by polar substituents, but also occurs without them.

Optical studies have proven[8] that the bonding capacity of copper in porphyrin complexes is wholly saturated by a single ligand. It would seem, therefore, that the loss of the hyperfine structure in basic solvents cannot be due to residual bonding between the pyridinated copper and the peripheral groups of a neighboring molecule. The conclusion is that e.s.r. hyperfine broadening in pyridine, and by extension in the other solvents as well, is primarily due to $\pi-\pi$ dimerization, and that the polar groups and other structural features exert only a secondary influence by affecting the degree of $\pi-\pi$ interaction. Whether this modifying influence comes about by an intermolecular or by an intramolecular mechanism cannot yet be determined.

It is interesting to note that Caughey and Corwin[17] found a second-order dependence on porphyrin concentration in the demetalation of copper etioporphyrin in acetic acid–sulfuric acid solution; the e.s.r. hyperfine structure of copper porphyrins is also broadened out in acetic acid.

The tendency to aggregation increases with polar side groups and exocyclic rings, but diminishes with chlorin unsaturation. This latter conclusion is based on the behavior of copper pyropheophorbide a, which gives a clear hyperfine in pyridine (unlike desoxophylloerythrin), but shows some broadening in acetone.

The hypothesis of $\pi-\pi$ aggregation readily explains why the behavior of the silver compounds differs from that of the copper series in pyridine. Because of the stronger association between the base and the metal in the second case, aggregation can then occur at only one face of the porphyrin plane, but with silver the basic solvent has an effect much like that of benzene, and $\pi-\pi$ interaction can take place on more sites. Otherwise there is little difference between the associative tendencies of silver and copper porphins under our conditions. In noninteracting solvents the latter seem to dimerize more firmly, but the reverse is the case when aggregation is due to strongly polar side groups in "active" solvents.

We conclude that the loose $\pi-\pi$ dimers which exist between solute molecules, particularly those with the structural features discussed above, may be dissociated by (i) interactions with certain extended π-systems (for example, by 1-bromonaphthalene but not by bromobenzene); (ii) interactions with hydrogen-bonding solvents (e.g., acetone); and (iii) in some cases, by the formation of pyridinate complexes with the metal of the porphyrin.

It has been deduced from spin resonance experiments

with copper uroporphyrin III[18] in various solvents that, in the dimers which cause the hyperfine broadening, the porphyrin molecules are placed parallel to each other, with the copper atoms directly opposite at a separation of 3.5 Å. Our discussions of the preceding paragraph as well as the results of Baker, Brookhart, and Corwin,[8] which prove that copper can bind only a single ligand, would indicate that there is no direct metal-metal interaction and that, indeed, the metal does not play a major role in this association phenomenon. The value of 3.5 Å. is consistent with interactions through the π-systems, if a π-cloud width of 3.4 Å. is assumed. This distance agrees with that measured on Stuart–Briegleb models and with the intermolecular porphyrin separation found by Tulinsky and Hoard.[19] It is somewhat less, however, than the closest Cu–Cu approach of 3.76 Å. reported by Fleischer[20] for copper tetraphenylporphin crystals.
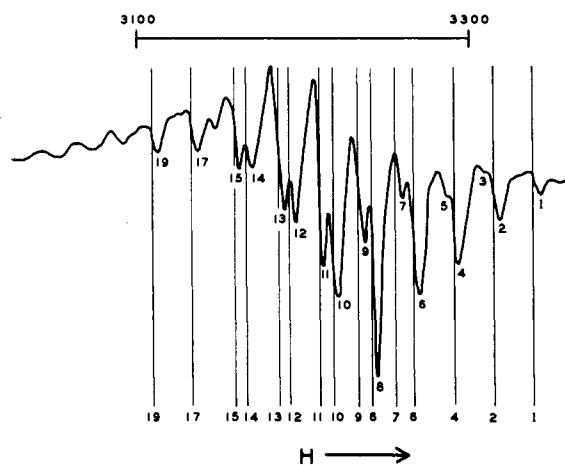

Figure 8. E.s.r. spectrum of silver deuterioporphyrin IX dimethyl ester, 0.001 M in castor oil at 77°K. The vertical lines indicate how the correspondingly numbered peaks are displaced in 0.001 M 1-chloronaphthalene solution at 77°K.; scale in gauss.

The changes in the electronic and spin resonance spectra of copper bisacetylacetonate and related compounds can be interpreted satisfactorily[21] by means of an energy level diagram in which the hybrid $*E_g$ levels of the metalloorganic system, to which the metal d_{xz} and d_{yz} orbitals contribute, are below the metal d_{xy} level. With this assumption, it is predicted that with increasing solvent interaction, $g_\perp$ would increase but that $g_{||}$ would remain constant or diminish slightly. In the spectrum of silver deuterioporphyrin IX dimethyl ester, however, where shifts in the value of $g_{||}$ can be determined with considerable precision (unlike the case of copper complexes), it was observed that $g_{||}$ also increased with greater solvent interaction, as may be seen from Figure 8. This shows that the displacement of the hyperfine lines toward low magnetic field

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Table II

| Copper complex | $g_\perp$ factors at 77°K. ($\pm$0.0003) | | |
	Acetone	1-Chloro-naphthalene	Pyridine
Desoxophylloerythrin monomethyl ester	2.0616[a]	2.0641[a]	2.0752[a]
Desoxophylloerythroetioporphyrin	2.0616[a]	2.0641[a]	2.0752[a]
Etioporphyrin II	2.0616	2.0643	2.0756
Pyrroporphyrin XV monomethyl ester	2.0627	2.0643	2.0747
Mesoporphyrin IX dimethyl ester	2.0624	2.0646	2.0753
Phylloporphyrin XV monomethyl ester	2.0633	2.0653	2.0761
Deuterioporphyrin IX dimethyl ester	2.0621	2.0657	2.0756
Protoporphyrin IX	b	b	2.0761
Tetraphenylporphin	b	2.0658	2.0776
Pyropheophorbide a monomethyl ester	2.0618[a]	2.0660	2.0776
Diacetyldeuterioporphyrin IX dimethyl ester	c	2.0668	2.0762[a]
Chlorin e-6 trimethyl ester	c	2.0681[a]	2.0835[a]
Dinitrodeuterioporphyrin IX dimethyl ester	c	2.0718	2.0930[a]

| Silver complex | g factors at 77°K. ($\pm$ 0.0003) | | | | |
| | Acetone | | 1-Chloronaphthalene | | |
	$g_{\parallel}$	$g_\perp$	$g_{\parallel}$	$g_\perp$	Pyridine
Mesoporphyrin IX dimethyl ester	2.1065	2.0305	2.1075	2.0322	c
Etioporphyrin II	2.1060	2.0304	2.1066	2.0325	c
Deuterioporphyrin IX dimethyl ester	2.1040	2.0294	2.1070	2.0317	c
Diacetyldeuterioporphyrin IX dimethyl ester		c		c	c

[a] Broadening. [b] Insoluble. [c] Complete broadening.

values, which accompanies a change in the solvent from castor oil to 1-chloronaphthalene, occurs on both the perpendicular and parallel sides of the spectrum. The arrangement of the molecular orbitals for these systems, therefore, must be one for which the B_{2g} orbital, to which d_{xy} of the metal contributes, is below that for the degenerate d_{xz} and d_{yz} levels. This arrangement was first proposed by Roberts and Koski for copper etioporphyrin II[3b] and more recently used to explain the spin resonance spectra of crystalline copper phthalocyanine.[3d] A summary of the g values found is given in Table II.

Volume Changes as a Criterion for Site Binding of Counterions by Polyelectrolytes[1]

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Exploratory measurements have been made of the volume changes accompanying the interactions between various polyelectrolytes containing sulfonate, carboxylate, phosphonate, or phosphate groups and a number of alkali and alkaline earth metal ions. With one exception, all the polyanions showed effects large enough to implicate site binding as the cause. Various structural features of the polyelectrolytes, such as the nature and the spacing of the anionic groups, the degree of dissociation, and the cross linking, were found to have a pronounced influence on the volume changes. The largest effects were observed with the long-chain polyphosphates. For the reaction $Li^+ + -PO_3^- \rightarrow -PO_3Li$, the volume increase ranged from 13 to 16 ml. per mole of participating lithium ion, depending on the over-all charge on the polyphosphate. In the case of analogous reactions of polyphosphate with sodium and magnesium ions, the corresponding ranges were 12.2 to 14.5 ml. per mole of Na^+ and 42 to 52 ml. per mole of Mg^{2+}. The method employed promises to be useful for studying the nature of site binding by polyelectrolytes and ion-exchange resins. Our results appear to be the most direct experimental evidence obtained so far for the role of the solvent postulated in theories dealing with cation sequences observed in a large variety of phenomena occurring in both synthetic and biological systems.