density at the iron to increase. This opposite electronic situation makes species I unstable toward the autoreduction. The solvent-dependent autoreduction found for $Fe(TPP)(OMe)_2^-$ in Me_2SO–MeOH is interpreted in terms of such H-bonding effects. This interpretation is in keeping with the findings by Del Gaudio et al.[37] that the autoreduction of $Fe(TPP)(Pip)_2^+$ is facilitated by the deprotonation of the coordinated piperidine.

In sum, it has been amply demonstrated that the d-orbital energy level of the low-spin complex $Fe(TPP)(OMe)_2^-$ is modu-

lated by the H-bond formation between the iron-bound MeO^- and the solvent MeOH. The H bonding weakens the axial ligand field, thereby causing alterations in electron density and reactivity at the central metal ion. The present model system is a simple example showing that heme reactivity is controlled by H bonding and as such, would help our understanding of electronic control of heme reactivity in various hemoproteins.

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Homo- and Heterodimer Formation in Metalloporphyrins

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The dimer formation constants in chloroform for CuP, AgP, and VOP, where P is mesoporphyrin IX dimethyl ester, have been obtained through EPR measurements at room temperature and spectral simulation. For CuP, measurements have been performed also in 1,1,2,2-tetrachloroethane and dichloromethane, and aggregation was found to be sensibly different in the three solvents. Heterodimer formation constants have been determined between the above metalloporphyrins and FePCl. Invariably the latter constants are larger than expected on the basis of the homodimer formation constants. The frozen-solution EPR spectra of CuP and AgP have provided the spectra of the pure dimeric species through computer manipulation. Evidence of two dimeric species is provided by the frozen-solution EPR spectra of VOP.

Introduction

It is well-known that porphyrins and metalloporphyrins tend to aggregate in solution. Several constants relative to dimer formation are available on porphyrins and metalloporphyrins in water solution and in organic solvents;[1,2] however, the factors determining the extent of dimer formation like the nature of the metal ion, the solvent, the planar or square-pyramidal geometry around the metal ion, and the kind of homo- or heterometallodimer are not yet fully understood. Owing to the relevance of this class of compounds as such and as models of naturally occurring metalloporphyrins, we thought it interesting to further investigate the tendency to aggregate of several metal derivatives of the mesoporphyrin IX dimethyl ester (MP hereafter) around room temperature in several solvents and to analyze the EPR spectra of the dimers at liquid-nitrogen temperature.

We have devised a procedure to determine the affinity constants for self-aggregation through EPR spectroscopy for those metal complexes that display EPR signals at room temperature such as the complexes of Cu^{2+}, Ag^{2+}, and VO^{2+}. Aggregation of such metalloporphyrins causes a decrease of the electronic relaxation times, and the EPR spectra at room temperature become very broad, possibly beyond detection. Therefore, the decrease in signal intensity of the monomeric species upon increase of solute concentration is related to solute aggregation. This holds also when a Cu^{2+}, Ag^{2+}, or VO^{2+} porphyrin interacts with a metalloporphyrin like mesoporphyrin IX dimethyl ester iron(III) chloride (FePCl), which does not show detectable EPR signal at room temperature. The latter derivative is five-coordinated with a chloride in the apical position of a square pyramid.[3]

Experimental Section

Metal-free mesoporphyrin IX dimethyl ester was provided by Sigma Chemical Co. and used without further purification. Its Cu(II), Ag(II), and Fe(III) complexes were prepared from the halides (Cu, Fe) or acetate (Ag) salts in dimethylformamide,[4] whereas the VO^{2+} derivative was

prepared from the acetylacetonate in phenol.[5] They were purified by thin-layer chromatography on silica gel using a mixture CH_2Cl_2/CH_3CN (98:2). The electronic absorption maxima and the EPR spectra of CuP and AgP are the same as those reported in the literature.[6-8] The absorption maxima and the molar absorbance of VOP and FePCl solutions fully agree with literature data.[9,10]

All the solvents were of analytical grade and were used without further purification.

The EPR spectra were recorded at X-band frequency with 100-kHz modulation on a Bruker ER200 spectrometer interfaced with the computer Aspect 2000 and equipped with a variable-temperature controller. The spectra of the solutions were recorded at 25 °C; particular care was taken to obtain highly reproducible spectra and intensities. Each spectrum was simulated in order to appreciate the line width. The spectra at liquid-nitrogen temperature of concentrated solutions have been recorded as glasses in 1,1,2,2-tetrachloroethane. The spectra of the monomeric species obtained on glasses of dilute solutions, when possible, were subtracted, after appropriate scaling, from those of the concentrated glasses, in such a way to have cleaner spectra of the dimeric species.

Results

Determination of Affinity Constants. For Homodimers CuP–CuP, AgP–AgP, and VOP–VOP. The EPR spectra were recorded at different concentrations of metalloporphyrin from 1×10^{-4} M to saturation ($\sim(2-6) \times 10^{-2}$ M). By taking into account the different gain when the spectra were recorded and by correcting for different concentrations, the same signal intensity would be expected for all the samples as if there were no concentration-dependent equilibria. Actually a sizable decrease in corrected intensity with increasing concentration is observed. Instead of the actual intensity measured through double integration of the signal, we have taken into consideration the height of either the hyperfine or superhyperfine splitted lines. Such heights should

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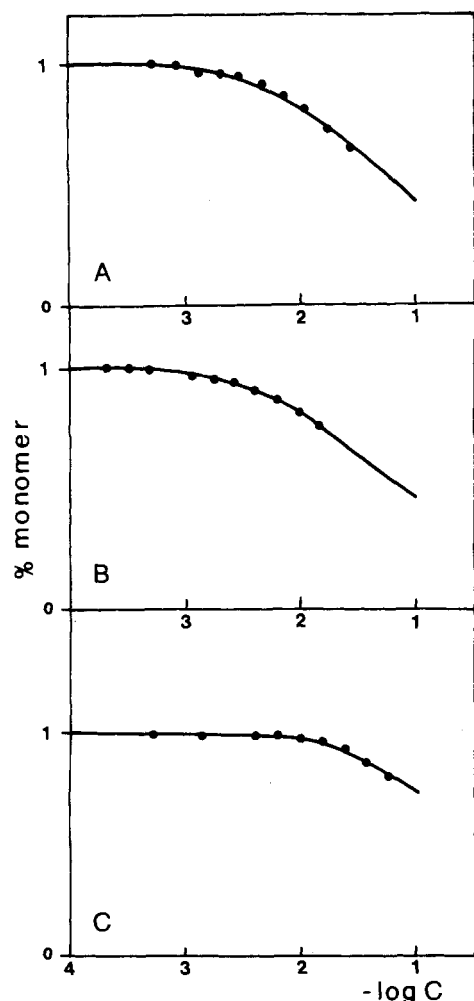
Figure 1. Patterns of the heights of the hyperfine (C) or superhyperfine (A, B) lines with concentration (chloroform solutions): A, CuP; B, AgP; C, VOP. The heights have been corrected in order to account for the different line widths (see text). Spectral parameters used for the line simulation: (A) A_N^{iso} = 1.60 mT, modulation amplitude (ma) 0.2 mT, line width variation from 0.94 to 1.34 mT at the extreme concentration values; (B) A_{Ag}^{iso} = 4.48 mT, A_N^{iso} = 2.24 mT, ma = 0.2 mT, line width variation from 0.8 to 1.1 mT at the extreme concentration values; (C) A_V^{iso} = 9.30 mT, ma = 0.5 mT, line width variation from 2.15 to 2.30 mT at the extreme concentration values. The solid lines are the best fitting curve of the corrected data points.

be minimally sensitive to possible underlying broad absorptions due to dimers. In Figure 1 the pattern of the heights of the hyperfine or superhyperfine lines with concentrations are reported for the investigated systems. By assuming a monomer–dimer equilibrium of the type

$$2MP \rightleftharpoons (MP)_2 \qquad (1)$$

and that the dimeric species does not affect the line height, the plots of Figure 1 can be used for determining the equilibrium constants. However, the line widths increase with increasing concentrations. This effect could be due to dipole–dipole interactions, spin-exchange phenomena, or chemical exchange. A temperature-dependent analysis of the lines has shown that the line widths of both concentrated and diluted solutions decrease with increasing temperature. A pattern is reported in Figure 2 for CuP. However, for the concentrated solutions the line width decreases less rapidly than for the dilute ones: this is against the operativity of dipole–dipole interactions since a reverse temperature pattern would be expected.[11] Both spin-exchange and chemi-
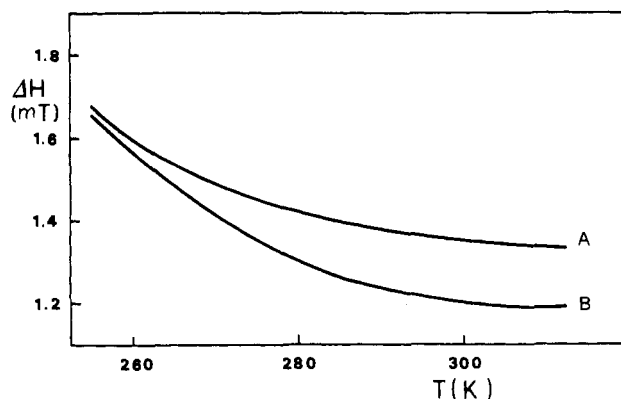
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Figure 2. Temperature dependence of the line widths of the superhyperfine lines in the EPR spectra of CuP solutions (ma 0.2 mT): (A) 2.88 $\times$ 10^{-2} M; (B) 1 $\times$ 10^{-3} M.

Table I. Dimer Formation Constants for the Homo- and Heterodimeric Species of Metallomesoporphyrin IX Dimethyl Ester

M_1	M_2	K, M^{-1}	σ
Cu	Cu	14.8	0.8
Ag	Ag	13.3	0.3
VO	VO	1.7	0.2
Cu	Fe	34.7	0.4
Ag	Fe	53.3	0.3
VO	Fe	11.4	0.5
Fe	Fe	<1	

cal-exchange phenomena are expected to follow a pattern similar to that observed; spin exchange is expected to become operative at higher concentrations than those used here. It is concluded therefore that the observed line broadening with decreasing temperature is mostly due to chemical exchange between monomeric and dimeric species, the exchange rate being in the quasislow region on the EPR time scale.

The observed spectra at various concentrations have been simulated with the same *g*, hyperfine and superhyperfine parameters, and varying line width. For example, the line width has been found to vary from 1.34 $\times$ 10^{-3} T for the 2.9 $\times$ 10^{-2} M solution of CuP to 9.4 $\times$ 10^{-4} T for the 1 $\times$ 10^{-4} M one.

This spectral simulation has allowed us to correct the heights of the EPR lines for different line widths by multiplying the observed heights by the ratio between the line width of the signals of the solution under examination and that of the most dilute solution. The calculated peak heights provide a set of values that are related to the amount of monomeric species and have been best fitted to obtain the constants for the above equilibria. Figure 1 shows that the experimental data can be accounted for on the above basis; it also shows that a monomer–dimer equilibrium is essentially what occurs in solution. The values of the affinity constants are reported in Table I.

For Heterodimers CuP–FePCl, AgP–FePCL, and VOP–FePCl. The experiments with solution mixtures of CuP–AgP, CuP–VOP, and AgP–VOP provided complex spectra due to the overlap of the two parent spectra. Their complexity prevented us from obtaining reliable intensity variation of the intensity of at least one monomeric species to be used for obtaining the heterodimer formation constant.

The above difficulties could be overcome when one metal ion of the heterodimer is a fast relaxing ion; in this case the EPR line of the latter is beyond detection at room temperature and does not complicate the spectra. We have measured the affinity constants for the heterodimers CuP–FePCl, AgP–FePCl, and VOP–FePCl.

If the experiment is performed by adding increasing amount of FePCl to a dilute solution of CuP, AgP, or VOP, the lines of

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Figure 4. EPR spectra of the $(CuP)_2$ dimeric species at 77 K in 1,1,2,2-tetrachloroethane obtained through computer difference between the spectra of a concentrated (inset) and a diluted CuP glass solution: (top) $\Delta M_s = 2$ region; (bottom) $\Delta M_s = 1$ region.
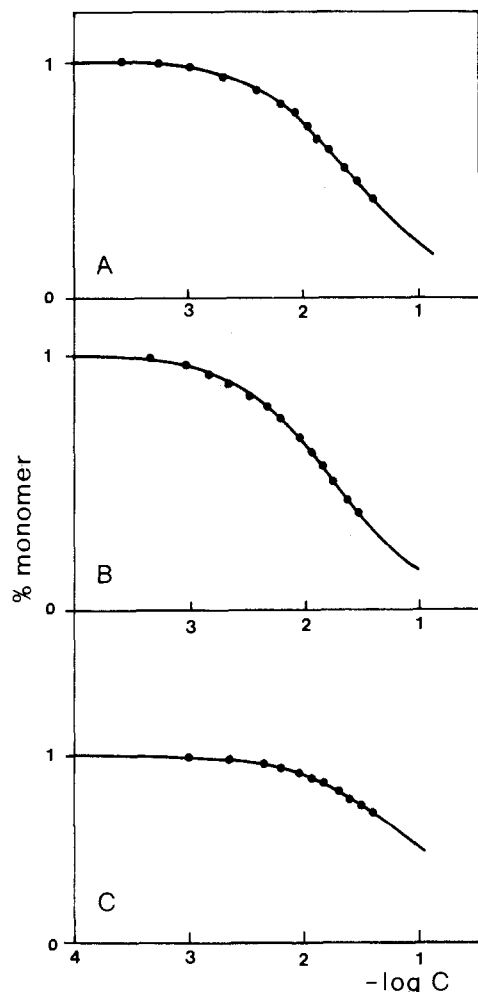
Figure 3. Patterns of the heights (corrected as described in the caption of Figure 1) of the hyperfine (C) or superhyperfine (A, B) lines with concentration: A, CuP + FePCl; B, AgP + FePCl; C, VOP + FePCl. Spectral parameters used for the line simulation: (A) $A_N^{iso} = 1.60$ mT, ma = 0.8 mT, line width variation from 1.25 to 1.40 mT at the extreme concentration values; (B) $A_{Ag}^{iso} = 4.48$ mT, $A_N^{iso} = 2.24$ mT, ma = 0.2 mT, line width variation from 0.81 to 0.90 mT at the extreme concentration values; (C) $A_V^{iso} = 9.30$ mT, ma = 0.5 mT, no change in line width (2.22 mT) within 2%.

the EPR signal of the latter metal ions decrease owing to the formation of heterodimer according to the equilibrium

$$MP + FePCl \rightleftharpoons MP-FePCl \qquad (2)$$
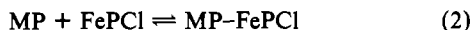
The concentration of CuP, VOP, and AgP solutions was chosen in such a way that the homodimer formation is negligible. The line width is only slightly affected by the presence of FePCl as shown by spectral simulation. The temperature dependence of the EPR line is quite similar to that of the dilute solution of the $S = ^1/_2$ metalloporphyrins. The absence of sizeable broadening is possibly ascribed to slower chemical exchange, consistently with the somewhat higher formation constants.

The corrected line heights were fitted with a program that calculates the affinity constants both for reaction 2 and for dimerization of FePCl (Figure 3; Table I). In all the cases the data provided a value for the latter constant <1 M^{-1}.

Measurements in Various Solvents. It would have been desirable to determine the constants for dimer formation in various solvents in order to better appreciate which parameters are capable of affecting the monomer–dimer equilibrium. However, the complexes are not soluble at appreciable concentrations in benzene, toluene, and acetone. They are soluble in nitrobenzene, but the large dielectric constant (35.7) did not allow us to perform measurements at various concentrations with the required precision and reproducibility. The complexes are soluble in *o*-dichloro-
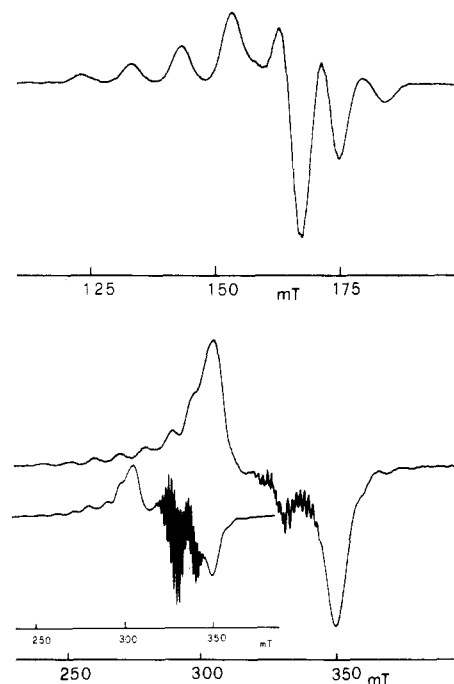
benzene; the EPR spectra of CuP solutions indicate that no detectable dimer formation occurs up to the maximum solute concentration of 5.2×10^{-3} M; by comparison of the data obtained in chloroform, it can be concluded that associated in *o*-dichlorobenzene is smaller than in chloroform. In 1,1,2,2-tetrachloroethane the constant relative to the $(CuP)_2$ formation is 5.0 $\pm$ 0.2 M^{-1}, i.e. quite less than in chloroform. In dichloromethane the above constant is 19.0 ± 1 M^{-1}.

The data are not numerous enough to relate the dimer formation constants with any solvent parameters. We can note that such constants are not related to the dielectric constant of the solvent (*o*-dichlorobenzene, ϵ 9.93; dichloromethane, ϵ 9.08; 1,1,2,2-tetrachloroethane, ϵ 8.20; chloroform, ϵ 4.81), contrary to previous suggestions.[1,15] This means that the relation between solvent properties and porphyrin aggregation is not simple.

EPR Spectra of Homodimer Species. The spectra of concentration solutions, recorded at 77 K, show strong signals due to the monomeric species and evidence of dimers, constituted by two series of signals, one centered at about $g = 4$ and the other in the $g = 2$ region. The spectra, beside the better quality, are essentially the same as those of this kind of porphyrin dimers previously reported.[6,12-14]

The spectra of the diluted glasses containing only monomeric species have been subtracted through computer manipulation after appropriate scaling from those of the concentrated glasses of the CuP and AgP complexes, in order to obtain cleaner spectra of the homodimers. Figures 4 and 5 indicate that such spectral manipulation can be quite successful.

The spectrum of the copper(II) dimer displays four sets of signals due to the fine structure of the dimer and a seven lines signal centered at 0.16 T due to the $\Delta M_s = 2$ transition. The first and the last of the four signal sets in the 0.24–0.38 T region are attributable to the parallel components of the two $-1 \rightarrow 0$, $0 \rightarrow 1$ transitions while the two inner ones are due to the perpendicular components of the same transitions. Each of the two parallel signals is split by the hyperfine coupling: one transition displays seven lines, the other displays only three, the other four being presumably covered by a perpendicular component. The hyperfine-splitted lines are spaced by 9.9 mT; this value is close to
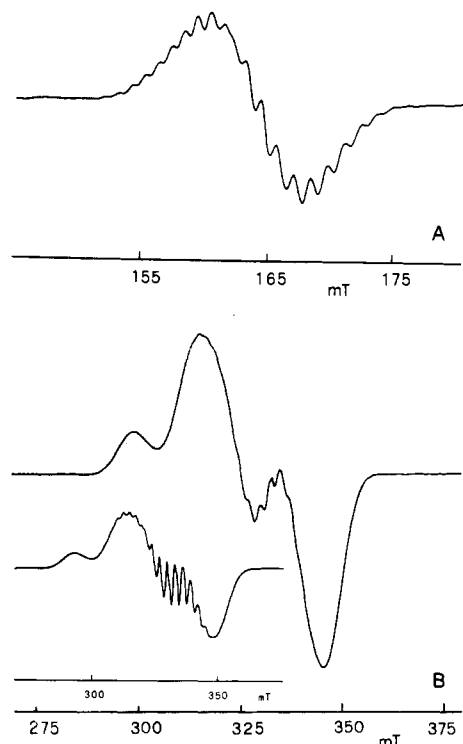
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Figure 5. EPR spectra of the $(AgP)_2$ dimeric species at 77 K in 1,1,2,2-tetrachloroethane obtained through computer difference between the spectra of a concentrated (inset) and a diluted CuP glass solution: (top) $\Delta M_s = 2$ region; (bottom) $\Delta M_s = 1$ region.

Table II. Spin Hamiltonian Parameters for the Monomeric and Homodimeric Species CuP and AgP

	$g_\parallel$	$g_\perp$	$A_\parallel$, 10^4 cm^{-1}	D,[a] 10^4 cm^{-1}
CuP	2.19	2.04	204	
CuP–CuP	2.18	2.06	99	414
AgP	2.11	2.03		
AgP–AgP	2.10	2.05		222

[a] From the splitting of the two parallel components of the $\Delta M_s = 1$ transition.

half of the value found for the monomeric species within the experimental uncertainty, as expected for weak metal–metal magnetic coupling.[15,16]

The spin Hamiltonian for two coupled $S = {}^1/_2$ ions, on the assumption of an axial symmetry, is

$$\mathcal{H} = g_z \beta H_z S_z + g_\perp \beta (H_x S_x + H_y S_y) + D[S_z^2 - {}^2/_3] + A_z S_z I_z + A_\perp (S_x I_x + S_y I_y) \quad (3)$$

From the separation between the two parallel components a value of D of 414×10^{-4} cm^{-1} can be read. Such a value is different from that previously reported because the spectrum was believed to show four parallel hyperfine lines at high field.[6] Such a D value, however, predicts the splitting of the perpendicular components to be 8% smaller than expected.[17,18] This gives an idea of the inadequacy of the usual first-order approach in evaluating the D parameter. The g values are almost equal to those of the monomeric species, as expected.[15,16] The $\Delta M_s = 2$ transition shows the expected seven-line pattern and is centered at a field value consistent with the above parameters. The spin Hamiltonian parameters are reported in Table II; they are consistent with earlier interpretation.[6,13,14]

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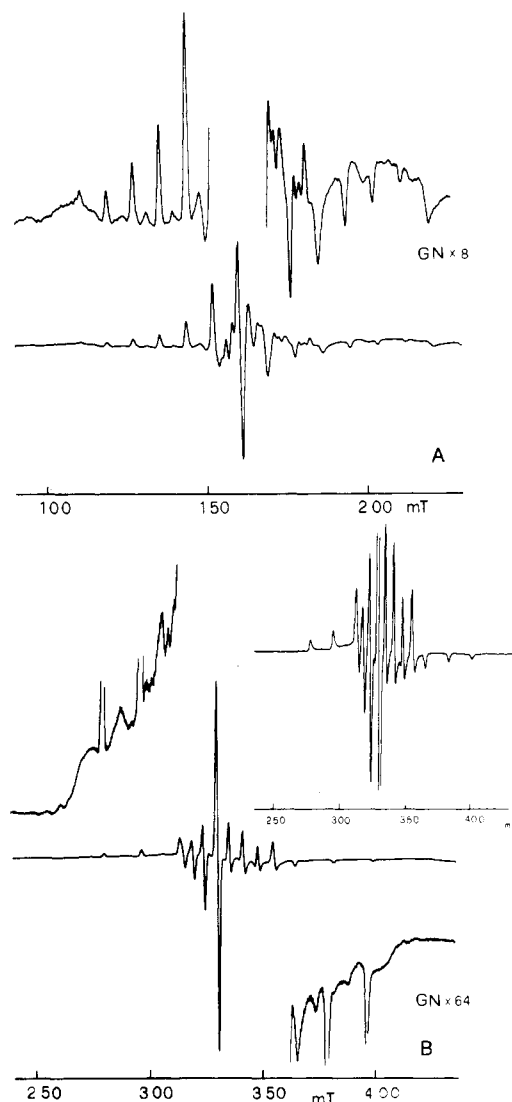
Figure 6. EPR spectra of concentrated and diluted (inset) solutions of VOP in 1,1,2,2-tetrachloroethane at 77 K; (A) $\Delta M_s = 2$ region; (B) $\Delta M_s = 1$ region.

The spectrum of the Ag(II) porphyrin dimer shows at least three well-shaped signals at 0.299, 0.316, and 0.346 T without any hyperfine splitting. The hyperfine splitting is not resolved. The low-field feature is attributable to a parallel component of the $\Delta M_s = 1$ transitions, the other presumably being under the high-field perpendicular component of the same transitions, at 0.346 T. The low-field perpendicular transition is centered at 0.316 T. A residual feature showing further splitting is present at 0.33 T; although we feel this is not due to computer manipulation, any assignment is not supported enough by evidence. Another signal centered at 0.163 T is observed and is attributable to the $\Delta M_s = 2$ transition; this signal shows a partially resolved superhyperfine structure. From the spin Hamiltonian (eq 3), the first-order parameters shown in Table II have been obtained, which are close to those earlier reported.[6] Again, from the D value estimated from the parallel transitions, a splitting of the perpendicular transitions 15% smaller than observed is predicted. The $\Delta M_s = 2$ transition occurs at a field consistent with that calculated from the spin Hamiltonian parameters reported in Table II.

The frozen-solution EPR spectra of concentrated solutions of VOP show evidence of dimer formation not only in the $\Delta M_s = 2$ region as previously reported for other porphyrins[14] but also in the $\Delta M_s = 1$ region. Furthermore the spectrum in the $\Delta M_s = 2$ region shows evidence of two overlapping spectra of different intensities (Figure 6). The amount of overall dimeric species is presumably very low, in agreement with the room-temperature formation constant. For this reason, and for the presence of at

least two dimeric species, subtraction of the spectrum of a dilute solution from that of a concentrated one has provided spectra with many ill-defined and weak absorptions, the interpretation of which has not been accomplished. The spectra of Figure 6 did not change upon further purification through chromatography of VOP, indicating that the weak signals were not due to impurities. On the other hand, the spectrum of diluted solutions of VOP even after drastic accumulation did not reveal any presence of impurity.

Discussion

The dimer formation constants of planar complexes $(CuP)_2$ and $(AgP)_2$ are essentially the same. Such values of 14 ± 1 M^{-1} compare with the value of 61.6 M^{-1} for $(NiP)_2$ and 30.9 M^{-1} for the pure mesoporphyrin IX dimethyl ester,[20] at almost the same temperature and in the same solvent. The latter values were obtained from NMR data that may also be sensitive to weaker, aspecific interactions among solute molecules. There is general consensus that the dimeric species detected through EPR spectroscopy are face-to-face type with direct metal–metal interaction.[6,14] This arrangement provided a metal–metal distance consistent with the magnitude of D. ^{1}H NMR intermolecular ring current shifts have been utilized extensively to determine the structure of porphyrin aggregates in solution,[19,21,22] leading to estimates of the distances between the planes that are twice or more than those found from EPR measurements.[1,21,22,29] The difference between dimer formation constants of CuP and AgP on one side and NiP on the other may depend on the different investigation technique and may not be meaningful in order to appreciate differences due to the metal ion. Differences in dimer formation constants due to different metal ions have been found in other metalloporphyrins.[23-25]

Square-pyramidal porphyrin derivatives like VOP and FePCl, on a purely statistical basis, are expected to give rise to dimer formation constants one-fourth of those of planar complexes. Such a constant for VOP is found to be 1.7 M^{-1}, whereas that for FePCl is estimated to be lower than 1 M^{-1}; both of them are definitely lower than expected. Again, extensive aggregate tetraphenylporphyrin iron(III) halides in solution has been elegantly detected in organic solvents by Snyder and La Mar through ^{1}H NMR relaxation measurements.[26] At intermediate concentrations the

structure of the dimer is proposed to consist of pairs of overlapping pyrroles in contact on the side of the porphyrin opposite to the out-of-plane iron. This confirms that NMR and EPR techniques detect different kinds of interactions among porphyrin moieties. The existence of at least two different species in addition to monomer has been proposed in the latter case. Although it has been proposed that metalloporphyrins can aggregate in different ways,[21,27,28] clear detection of two dimeric species has not been reported. It is quite unfortunate that the low intensity of the EPR signal of the two VOP dimers with respect to the monomeric species has not allowed us to pursue the investigation of the possible structural differences between these two species.

Heterodimer formation constants in planar metalloporphyrins, on a purely statistical basis, are expected to be 2 times those of homodimeric species; if the parent species are planar and square-pyramidal, respectively, the affinity constant is expected to be equal to that of the homodimer between planar species. The observed values for CuP–FePCl and AgP–FePCl are definitely larger than expected. The heterodimer formation constant for VOP–FePCl is expected to be equal to $2(K_1K_2)^{1/2}$, and again it is found more than twice larger than expected.

In conclusion this research has provided additional homodimer formation constants for planar Cu(II) and Ag(II) metalloporphyrins. Solvent effects on such constants do not agree with previous suggestions, indicating that there is not a simple relationship between solvent properties and tendency of the solute to aggregate. For the first time, homo- and heterodimer formation constants involving square-pyramidal porphyrins have been estimated. The homodimer formation constants between square-pyramidal porphyrins are very small, whereas the heterodimer formation constants are substantially favored with respect to expectation. From the frozen-solution spectra of concentrated solutions of CuP and AgP the spectra of the homodimer species have been obtained, which have allowed a more precise reading of the transitions and a more critical estimation of the spin Hamiltonian parameters.

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