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EPR EVIDENCE FOR DIMER FORMATION OF Cu(II)TETRA(4-SULFONATOPHENYL)PORPHYRIN SODIUM SALT IN AQUEOUS SOLUTIONS

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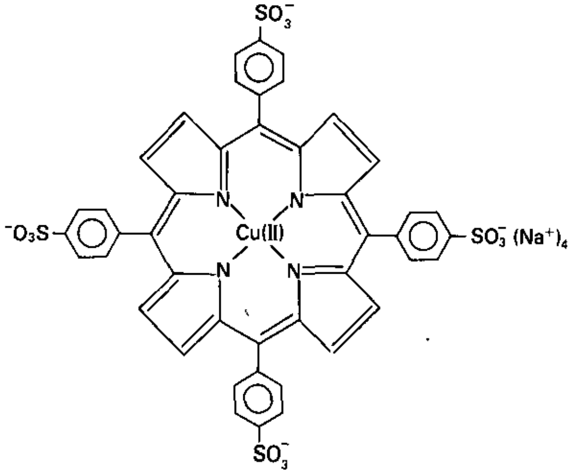
EPR evidence is presented to show, for the first time, that the water soluble meso-aryl-porphyrin Cu(II) complex forms a non-covalent tight dimer. Analysis of the spectrum gave the Cu-Cu distance (4.9A) and the angle between the $g_{\parallel}$ axis and the Cu-Cu axis (33°). Mode of interaction of added imidazole with the aggregates is also discussed.

Aggregation of porphyrins and metalloporphyrins has been the subject of extensive spectroscopic studies for some time.[1] Knowledge of association in solution has evolved from the undefined aggregated state assumed in early days, to a well-defined dimer formation proven recently in an increased number of cases.[2] The formation and the structure of a covalently linked μ-oxo type dimer as found in Fe(III)-porphyrins are well established,[3] but the characterization of the non-covalent dimers, in contrast, appears still unsatisfactory due to the variety of factors influencing the intermolecular association and solvent interactions.

For example, it has been generally believed that meso-aryl-porphyrins do not form a dimer of the latter type, because of steric hindrance of the out-of-plane aryl groups.[4] Snyder et. al.[5], however, reported recently on the NMR relaxation of tetra-p-tolyl-porphyrins in organic solvents, and concluded that these compounds do form a specific non-covalent dimer. The structure of the dimeric species has not been quantitatively defined, but the proposed model indicates a relatively long metal-metal distance, probably, $\gtrsim$ 7A. Also, the water soluble metallo-porphyrins were thought to exist in monomeric form in an acid or neutral solution.[6] Lately, temperature-jump kinetic studies by Krishnamurthy et al.[7] have shown that many of the water soluble meso-aryl-porphyrins actually form dimers, although the species have not been identified in most cases.

We present in this communication unequivocal evidence for the formation of a tight dimer of Cu(II)tetra(4-sulfonatophenyl) porphyrin (I) in aqueous solution and the results of investigations on the related aggregation behavior.



(I)

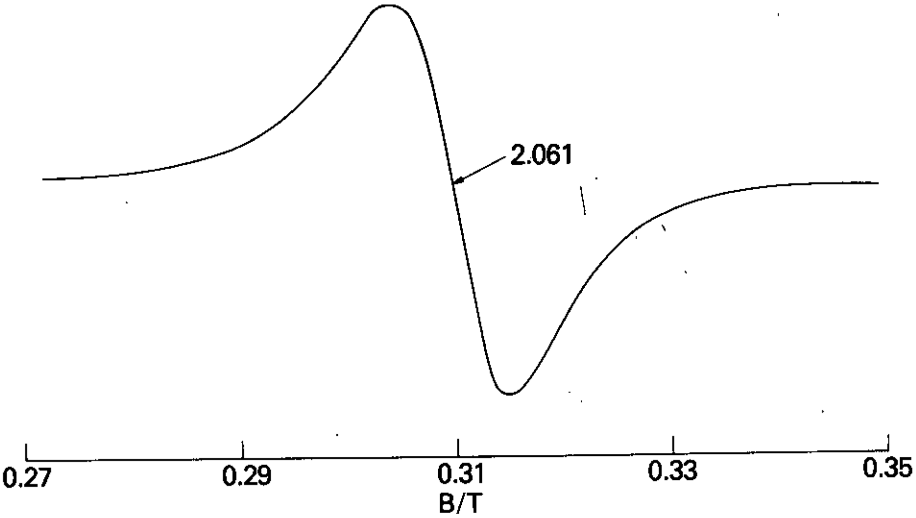


FIGURE 1 EPR spectrum of (I) at 28K. Concentration = 4.47 x 10^{-3}M, pH = 7 (0.05 M phosphate buffer).

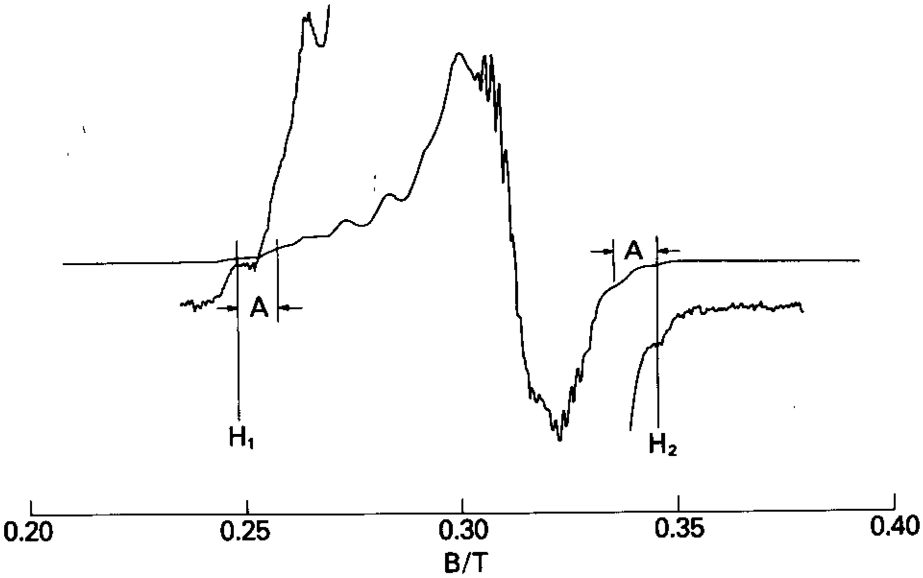


FIGURE 2 EPR spectrum of (I) under the same condition as in FIG. 1, but added with ethylene glycol (1:1 v/v).

In Fig. 1 is shown an EPR spectrum of (I) (conc. = 4.47 x 10^{-3}M) in frozen solution of pH 7 Na phosphate buffer (0.05M) observed at 28K. The broad signal (peak-to-peak width = 0.0109T; the magnetic field is measured in units of a Tesla = 10^4 Gauss) exhibits no feature due to g anisotropy or Cu nuclear hyperfine structure, and evidently, represents a higher order aggregate with exchange interaction strong enough to average out the anisotropy. Dilution of the same solution by 100-fold essentially does not change the spectrum.

Addition of ethylene glycol to the solution (1:1 v/v) causes partial dissociation of the aggregates as shown by the monomeric and dimeric components in the spectrum in Fig. 2. Also shown is the so-called ΔM=2 spectrum at half-field (~ 0.15T), having seven hyperfine components, which is an unmistakable sign of the formation of a well-defined dimer (Fig. 3). The approximate zero-field splitting (D_2) of the ΔM = ± 1 transition can be estimated from the peaks H_1 and H_2 at the low and the high

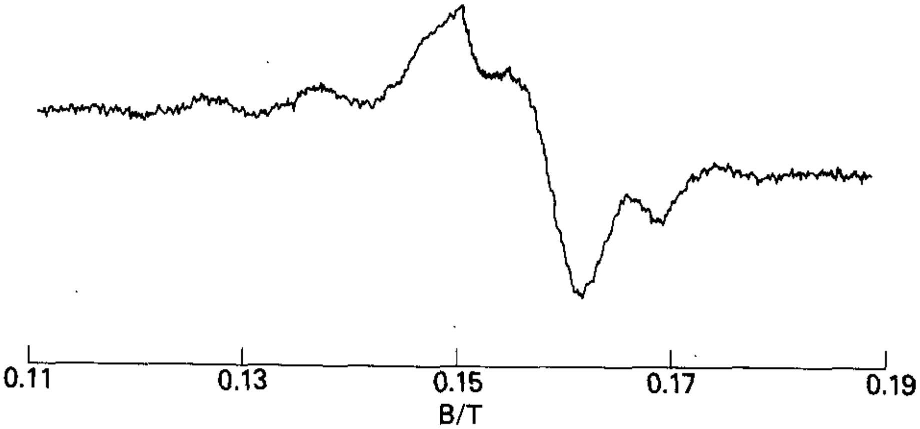


FIGURE 3 EPR spectrum of (I) in the half-field region, the conditions are the same as in FIGURE 2.

field ends of the spectrum, respectively

$$D_2 = (1/2)(H_2 - H_1 - 6A) = 0.0525T = 263 \times 10^{-4}\mathrm{cm}^{-1}$$

The D_2 can also be related to Cu-Cu distance r by[8]

$$D_2 = 0.65 g_2^2 / r^3$$

where $g_2 = h\upsilon / [(1/2)(H_2 + H_1)\beta] = 2.150$, $h\upsilon$ is the microwave quantum, and β the Bohr magneton. The Cu-Cu distance thus calculated is 4.9Å. We note that the g_2 value of 2.150 is significantly smaller than the $g_{\parallel}$ value (2.188) of the monomer which was observed for Cu(II)(tetraphenylporphyrin) in the host crystal of H_2(tetraphenylporphyrin). This indicates that the Cu-Cu axis is substantially deviated, with the angle ξ, from the normal to the porphyrin plane.[8] Using the approximate relation

$$g_2^2 = g_{\parallel}^2 \cos^2\xi + g_{\perp}^2 \sin^2\xi$$

ξ is estimated at approximately 33°. These structural parameters, although obtained using some approximation, establish the dimer configuration of (I) to be that of a tight dimer rather than the one with a long metal-metal distance. This distance, however, is somewhat longer than those (4.16 - 4.24A) obtained similarly for the dimers of Cu(II)(meso-nitro-octaethylporphyrin) and the analogues in frozen toluene solution.[9] The difference may be attributed to the repulsive interaction caused by the net negative cnarge as well as some steric interference.

We also note that the EPR spectrum of Cu(II)(tetraphenylporphyrin in chloroform or toluene does not show any indication of a dimer, although formation of the one having a long Cu-Cu distance can not be ruled out. The distinction from the present water soluble porphyrin can be explained by an increased degree of solvation around the porphyrin in organic solvents, whereas in (I) in aqueous solution, the hydration would take place mostly in the polar periphery, leaving the porphyrin π-system open to the intermolecular

π-π interaction.

Dissociation of metalloporphyrin aggregates is known to be efficiently effected also by imidazole, which is generally considered to act as an axial ligand to the metal ion. In the present system, however, the addition of imidazole to the neutral solution of (I) in 100-fold excess only barely affects the EPR spectrum of the aggregate. It takes 500 fold or more of imidazole to see a substantial dissociation, and even then, the signal due to the dimer persists at both ends of the monomer spectrum as well as in the half-field region. Comparison shows that the EPR spectrum of the dimer under this condition is identical to that resulting by adding ethylene glycol. Also, the $g_{\parallel}$ value of the monomer in the presence of imidazole is the same as the value of Cu(II)(tetraphenylporphyrin) quoted above. These facts indicate that imidazole does not bind to Cu(II) ion in the monomer (and probably, neither in the dimer), since the axial ligation is known to cause changes in g values and in hyperfine coupling constants. Thus the dissociation may be achieved through imidazole-porphyrin π-π interaction competing against the interaction between the porphyrin molecules.

Addition of Na laurylsulfate or methanol, which causes dissociation in pyrrole-substituted porphyrins, was found ineffective in the present meso-substituted porphyrin.

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