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SURFACE-ACTIVE PORPHYRINS

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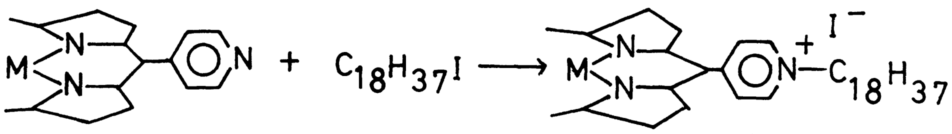
A series of cationic surface-active porphyrins were synthesized, and their micellar formations in organic solvents were confirmed by spectroscopy.

Both micelles and layers are of fundamental consequence for pure and applied chemistry. Syntheses of new type surfactants must, therefore, be regarded as important. On the other hand, porphyrin compounds are well known with their wide variety of functions as complex catalyst, EDA catalyst, dye, sensitizer, oxygen carrier, electron carrier and so on. In this letter, I wish to report the synthesis of a series of surface-active porphyrin complexes and the spectroscopic evidences for their formation of reversed micellar colloids in organic solvents.

Preparation:



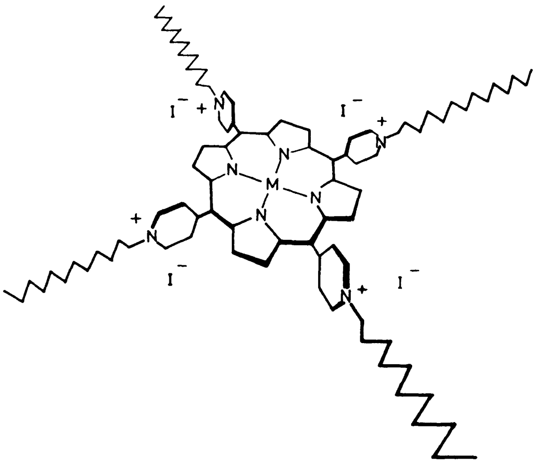


Fig. 1. MSt_4PyPI_4; the schematic structure.

Following the above equation, meso-tetra(4-N-stearylpyridyl)porphyrin tetraiodide complexes (abb. MSt_4PyPI_4; where M = Mg^{II}, Zn^{II}, Co^{II}, Cu^{II} and $Mn^{III}(OH^-)$. see Fig. 1) were synthesized. The tetrapyridylporphyrin complexes (TPyPM; where M = Co^{II}, Cu^{II} and Mn^{III} (CH_3COO^-)), the starting materials, were obtained by the usual method$^{1)}$ from the metal free base ($TPyPH_2$) and the metal acetates. TPyPZn was synthesized by the use of Fleischer's method$^{2)}$, and TPyPMg referring to the Buchler's method for the preparation of

Table 1. Analytical data (figures in parentheses are those calculated).

compounds	C	H	N
$Mg^{II}St_4PyPI_4 \cdot H_2O$	61.70 (61.72)	8.24 (8.04)	4.72 (5.14) %
$Zn^{II}St_4PyPI_4$	60.86 (61.04)	7.84 (7.87)	4.94 (5.08)
$Co^{II}St_4PyPI_4 \cdot 4H_2O$	59.22 (59.28)	7.96 (8.20)	5.22 (4.94)
$Cu^{II}St_4PyPI_4 \cdot 2H_2O$	59.85 (60.13)	7.47 (7.87)	4.74 (5.01)
$Mn^{III}(OH^-)St_4PyPI_4 \cdot H_2O$	60.15 (60.36)	8.24 (7.84)	5.14 (5.03)

octaethylporphinemagnesium (OEtPMg)$^{3)}$. The thermal coupling reactions between TPyPM and stearyliodide were run at 115° C for 4 days under Ar atmosphere in trichlorobenzene, which is the dispersing agent. The crude compounds were purified repeatedly on alumina columns (grade III) using chloroform-methanol system as the mother solvents and/or the eluents. Final yield, ≲40%. Analytical data, see Table 1. The completion of the reaction and the chromatographical purification were confirmed using the frequency shift of the ν_{CN} stretching mode of the pyridine ring as the monitor. It changes from about 1600 cm^{-1} of pyridine ring to about 1640 cm^{-1} of pyridinium ring, as the reaction or the purification proceeds.

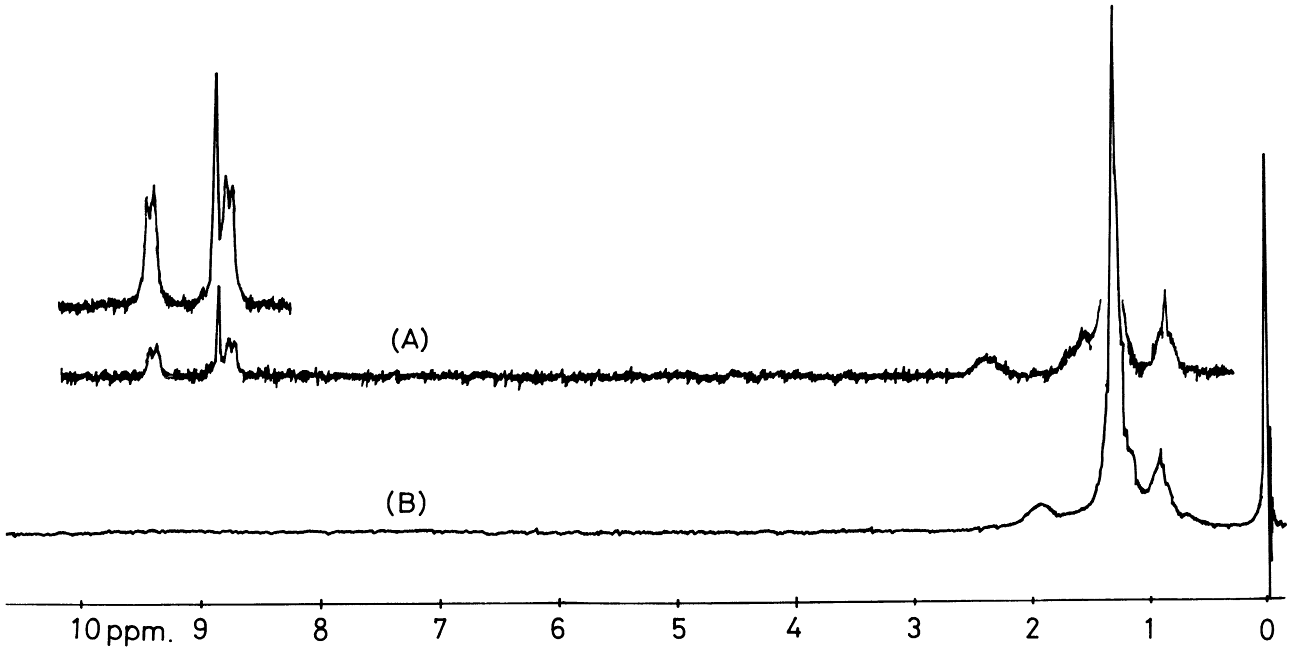


Fig. 2. ^{1}H-NMR spectra of $Mg^{II}St_4PyPI_4 \cdot H_2O$ in the mixed solvent of N,N'-dimethylformamide-d^7, methanol-d^4 and chloroform-d^1 (1 : 1 : 1) --- (A), and in chloroform-d^1 --- (B).

Aggregation: Figure 2 shows the ^{1}H-NMR spectrum of $Mg^{II}St_4PyPI_4 \cdot H_2O$ in deuterated chloroform compared to that in a mixed polar solvent. In the mixed solvent, we can see three kinds of ring protons; one is for the porphyrin ring proton --- δ = 8.88 ppm, and the others are for pyridinium ring protons --- δ = 8.74, 8.80, 9.40, 9.46 ppm / TMS. But, in chloroform, these ring protons are not presenting themselves and only the methylene protons and methyl protons of the hydrocarbon chains are observed. This result is the simple evidence for the fact that $Mg^{II}St_4PyPI_4 \cdot H_2O$ solves in chloroform to form a reversed micellar colloid. In the colloid, the ring protons are placed in the center, and their motions are hindered by the packing. The hydrocarbon chains, which surround this hydrophilic center, are fluctuating in the solvent forming a hydrophobic mantle.

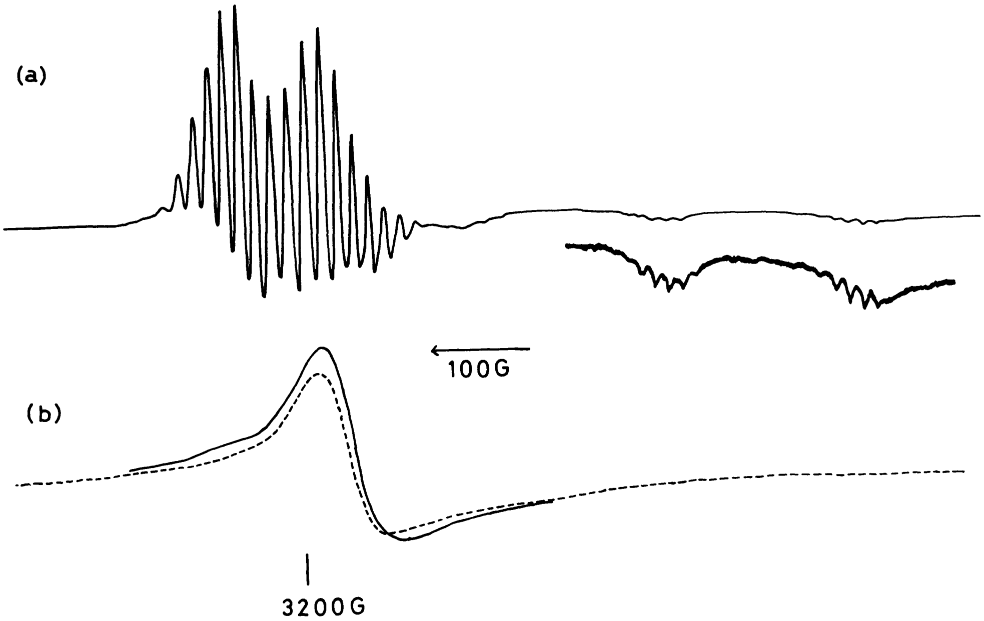


Fig. 3. The comparison of the Cu^{II} ESR spectra; (a) --- $Cu^{II}St_4PyPI_4 \cdot 2H_2O$ in N,N'-dimethylformamide, (b) --- $Cu^{II}St_4PyPI_4 \cdot 2H_2O$ in chloroform.

The evidence for the aggregation of the dye-surfactant which has a paramagnetic ion in its center is obtainable using ESR spectroscopy. In Fig. 3, two types of ESR spectra of $Cu^{II}St_4PyPI_4 \cdot 2H_2O$ are given; (a) is for the copper dye in N,N'-dimethylformamide, and (b) for that in chloroform ($\sim 10^{-3}$M). Signal (a) is giving the typical spectrum for a monomeric copper porphyrin, which has two kinds of hyperfine structures due to one copper(I = 3/2) and four nitrogen(I = 1) atoms$^{4)}$.

On the contrary, the hyperfine structures are not presenting themselves in the spectrum (b). According to the work for surface-active manganese complexes$^{5)}$ by Kitahara et al., the result is explained by the dipolar broadening upon the reversed micellar formation. That is to say, as the association in chloroform proceeds, the central copper ions become to interact magnetically with each other, and this magnetic dipolar interaction becomes so strong as to cover the hyperfine interactions with the formation of the micelle. A similar dipolar broadening was observed also for $Mn^{III}(OH^-)St_4PyPI_4 \cdot H_2O$ in chloroform, and the signal was a singlet of neither Lorentzian nor Gaussian having the width 462 G for peak-to-peak value. But, as for the cobalt compound, no ESR signal was observed at room temperature due to its short spin-lattice relaxation time, as found in cobalt tetraphenylporphyrin$^{4)}$ and cobalt phthalocyanine$^{6)}$.

The metallo-dye surfactants become monomeric in such polar solvents as N,N'-dimethylformamide, acetonitrile and methanol. On the other hand, they form reversed micellar colloids in comparatively weak polar solvents such as chloroform and dichloromethane, or the mixed solvents of them with non-polar solvents. Considering the molecular structure of the surfactants, I propose a lodlike structure for the shape of the micelles. In the center of the colloid, there will be a one-dimensional or helical piling of the porphyrins, and around them, the core of hydrophilic pyridinium moieties, which are enclosed and isolated from other colloids by the mantle of the fluctuating hydrocarbon chains.

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