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AGGREGATION STRUCTURE OF PORPHYRIN MODEL COMPLEX 4,4'-DIHEXYL-N,N'-DISALICYLIDENE-ETHYLENEDIAMINENICKEL(II) IN CHLOROFORM-d_1 SOLUTION STUDIED BY ^{1}H NMR SPECTRA

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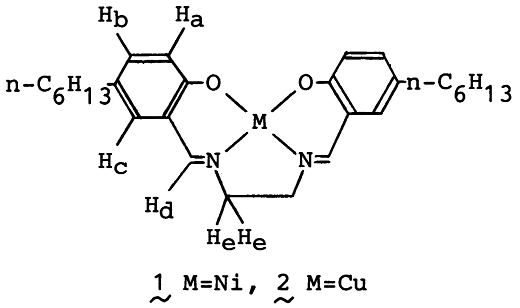
^{1}H NMR peak shift due to aggregation was observed in chloroform-d_1 solution of porphyrin model complex, 4,4'-dihexyl-N,N'-disalicylidene-ethylenediaminenickel(II) (**1**), and a piled structure was proposed for the aggregate of **1** from the sign and the amount of the shifts.

The importance of aggregation in the field of coordination chemistry has been recognized recently from the studies on chlorophylls,$^{1)}$ vesicles,$^{2)}$ and others.$^{3)}$ In particular, the intensive studies on the chlorophyll aggregate suggested its difference from monomeric species and its significant role in photosynthesis.$^{4)}$ As a new attempt to investigate the aggregation phenomena of metal complexes, we introduced alkyl chains to the metal complexes. The introduction of alkyl chains causes an increase in their solubility in organic solvents, such as chloroform, so that it becomes easier to investigate their behaviour in the solution. The increase in solubility gives an extra occasion for the complex to aggregate, and is effective in maintaining the aggregate in the solution. In the course of our investigation, a concentration dependence in ^{1}H NMR spectra due to aggregation was observed for complex **1**.

Complex **1** was obtained readily by refluxing an ethanolic solution of nickel(II) acetate, 1,2-diaminoethane, and hexyl substituted salicylic aldehyde in a molar ratio of 1:1:2. Complex **1** precipitated upon cooling and was recrystallized from ethanol-chloroform mixture. Found C,68.17; H,7.76; N,5.88%. Calcd for $C_{28}H_{38}N_2NiO_2$: C,68.17; H,7.76; N,5.68%. Complex **1** in chloroform (2×10^{-4} mol dm^{-3}) gives an absorption spectrum similar to that of the non-substituted complex with a slight red shift (500 cm^{-1}).$^{5)}$ As the corresponding



1 M=Ni, **2** M=Cu

copper(II) complex, 4,4'-dihexyl-N,N'-disalicylidene-ethylenediaminecopper(II) (2) also exhibited such a shift (1000 cm^{-1}),[6] and the concentration, at which the electronic spectra were measured ($2x10^{-4}$ mol dm^{-3}), was far below the region of aggregation, it is concluded that complex 1 takes the square-planar coordination, and that the red shift observed is due to the electronic effect of the substituted hexyl groups.

The ^1H NMR spectra of 1 in chloroform-d_1 were measured by 90 MHz Hitachi R-40, and all peaks were assigned by their coupling patterns. On increasing the concentration, the signals assigned to the protons at 3-positions of benzene rings (H_c) and those of azomethine group (H_d), clearly showed up-field shifts (Fig. 1). The shifts were observed only for H_c and H_d, and neither aliphatic protons nor protons at 6- (H_a) and 5-positions (H_b) of benzene rings showed observable shifts. These up-field shifts become conspicuous from the concentration of ca. 10^{-3} mol dm^{-3}, and moves ca. 0.5 and 0.6 ppm upwards for H_c and H_d respectively, until the solution saturates at 0.29 mol dm^{-3}.

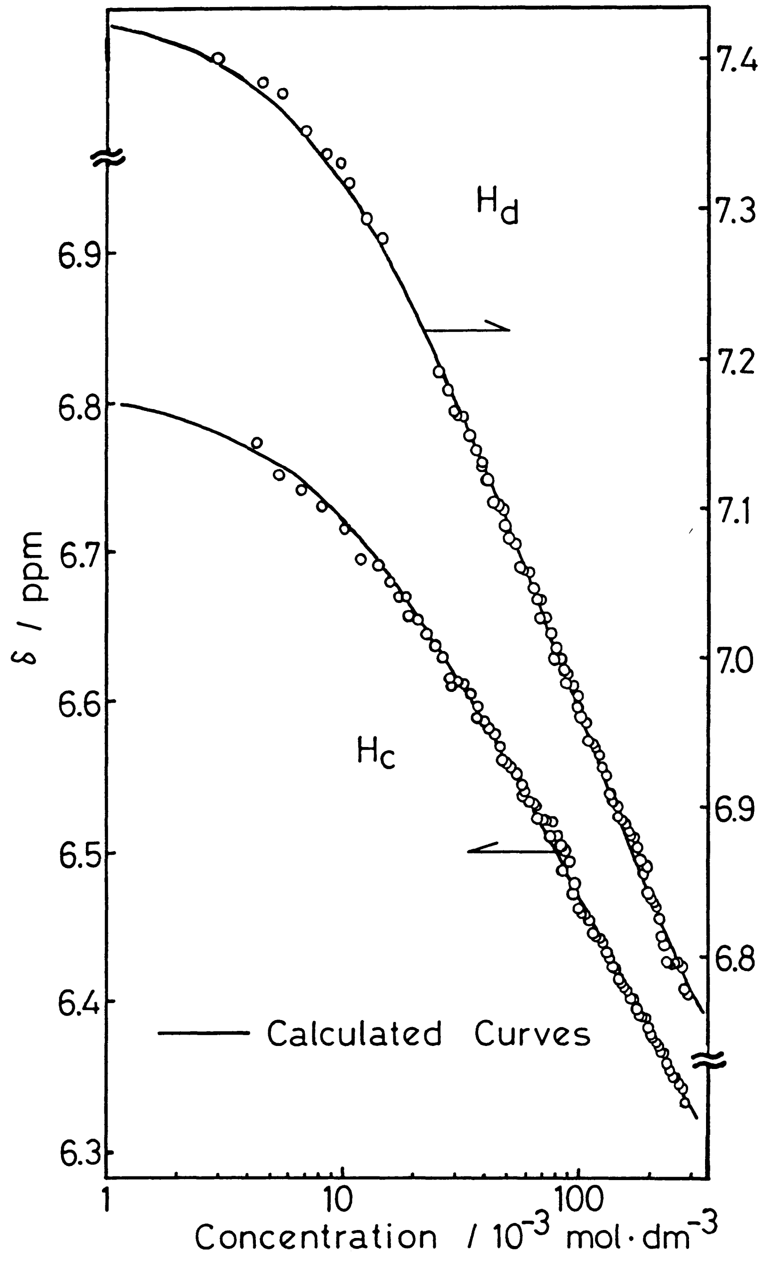


Fig. 1. Concentration vs. chemical shifts of H_c and H_d of 1 in chloroform-d_1 at 35 °C.

The up-field shifts can be attributed to the aggregation of the complex. When the proton is located above an aromatic ring, its ^1H NMR signal shifts to an upper field due to the effect of ring current in the aromatic ring. Thus, in the aggregate of 1, the benzene ring of 1 should be placed above the protons H_c and H_d of another molecule of 1, and vice versa. As the ^{1}H NMR spectrum of **1** exhibits the shift without splitting, there exists a rapid equilibrium between the aggregate and the monomeric species.

Further, the equilibrium constant of aggregate formation can be estimated from the concentration dependence of the shift. Assuming an equilibrium between monomer and dimer for the first order approximation, the chemical shift for a given proton (δ) at any concentration (C) can be given as

$$\delta=\delta_d+(\delta_m-\delta_d)(\sqrt{1+8CK}-1)/4CK$$

where K, δ_m, and δ_d stand for equilibrium constant (=[dimer]/[monomer]^2), chemical shifts of monomer and dimer, respectively. Calculations to fit the theoretical curves to the observed data of H_c and H_d were performed, and the curves given in Fig. 1 were obtained with the value of δ_m=6.81, δ_d=6.06 for H_c, δ_m=7.44, δ_d=6.37 for H_d, and K=7.5 dm^3 mol^{-1}. Porphyrin complexes, such as chlorophylls, also show this kind of up-field shifts,$^{7)}$ and their equilibrium constants are in the same order as the K value obtained here. This fact indicates that complex **1** has a similar aggregating ability to that of the porphyrin complexes.

That the ligand of **1** is a hexyl derivative of N,N'-disalicylidene-ethylenediamine, usually abbreviated as salen,$^{8)}$ the cobalt complex of which is known as a good model for hemoglobin by its oxygen coordinating nature.$^{8)}$ However, the ^{1}H NMR of the non-substituted salen complex exhibited no observable shift. This is probably because the solubility of this complex is far lower than the concentration at which the complex aggregates, or in other words, because the crystallization takes place prior to the aggregation in the case of [Ni(salen)]. It is apparent, therefore, that the effect of aliphatic side chains is to increase the solubility of the complex in chloroform, and to reveal the ability to aggregate in the solution, which was unobservable with the metal complex of low solubility.

Another information on aggregation phenomena was obtained from the investigation on the paramagnetic broadening of ^{1}H NMR spectra caused by adding the corresponding copper(II) complex **2** to a chloroform-d_1 solution of **1**. Here again, the spectra of the protons H_c and H_d were broadened seriously, and

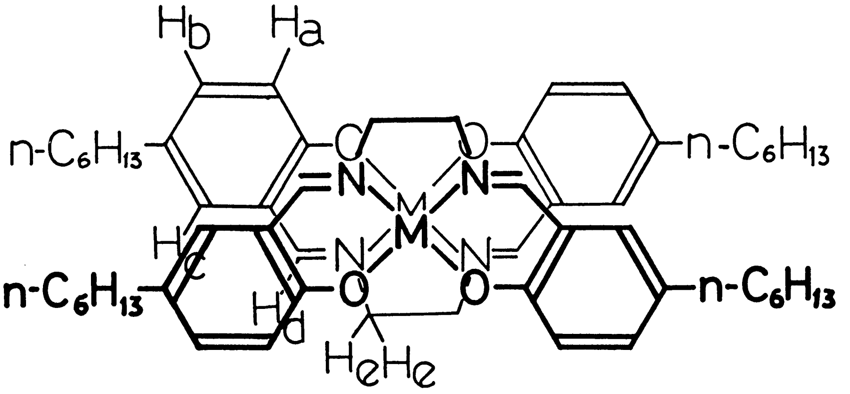


Fig. 2. The structure proposed for the aggregate of **1**.

further, the methylene protons of 1,2-diaminoethane moiety (H_e) were strongly affected. The intensity of the broadening observed was in the order of $H_e \approx H_d > H_c >$ other protons. As the paramagnetic broadening is caused by the unpaired electron of copper(II), the structure of **1**-**2** aggregate must be as such that copper(II) of **2** is placed near the protons H_c, H_d, and H_e. Considering that the structures of **1**-**1** and **1**-**2** aggregates are not so different, the structure of the aggregate in these systems can be given as that in Fig. 2. This structure proposed for the aggregate of **1** in chloroform-d_1 solution is quite different from that obtained for the crystal of [Cu(salen)] $CHCl_3$ by the crystallographic study.[9] The dimer in the crystal has weak apical bonds between copper(II) of a [Cu(salen)] molecule and coordinating oxygen atoms of another molecule in the dimer.

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5) Electronic Spectrum. $\varepsilon_{max}(\lambda_{max})$=170 $dm^3mol^{-1}cm^{-1}$ (554 nm), 7180 $dm^3mol^{-1}cm^{-1}$ (422 nm), 9290 $dm^3mol^{-1}cm^{-1}$ (348 nm). The second peak has two shoulders at both sides, and the last peak has a shoulder at shorter wavelength.
6) Electronic Spectrum. $\varepsilon_{max}(\lambda_{max})$=430 $dm^3mol^{-1}cm^{-1}$ (565 nm), 10660 $dm^3mol^{-1}cm^{-1}$ (379 nm). The second peak has two shoulders at both sides. Elemental analysis. Found: C,67.83; H,7.21; N,5.74%. Calcd for $C_{28}H_{38}CuN_2O_2$: C,67.51; H,7.69; N,5.62%.
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