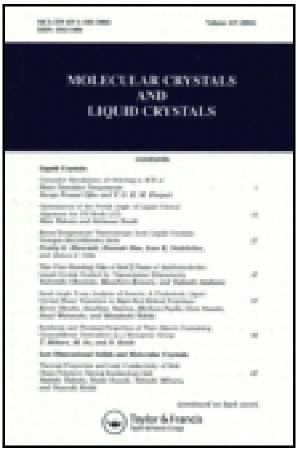

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Weak Exchange Interaction of Copper(II) Pairs in Rigidly Linked Porphyrin Dimers

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In a series of gable-type di-copper(II) porphyrin dimers as well as the corresponding mono-copper(II)-free base porphyrin dimers, Electron Paramagnetic Resonance (EPR) spectra are measured in toluene at 77 K and 300 K, in order to clarify spin-spin coupling between the two metal spins. By comparison of the EPR data obtained in fluid solution and rigid media, we have separated contribution of exchange interaction from that of dipole-dipole coupling, which is averaged out under the fluid condition by the molecular rotational diffusion. On the basis of the line-shape analysis of the EPR spectra, the magnitudes of exchange interaction are evaluated as $0 – 3 \times 10^{-3}$ cm^{-1}, depending upon the spacer unit. The observed spacer dependence of exchange coupling provides a clear evidence of through-bond mechanism.

Keywords: electron paramagnetic resonance; copper(II) porphyrin dimers; spin-spin coupling; through bond; spacer dependence; molecular tumbling

INTRODUCTION

Spin-spin coupling between the two spin centres plays one of the most important roles in determining magnetic properties of metal complex assemblies, where the paramagnetic metal centres are distanced by

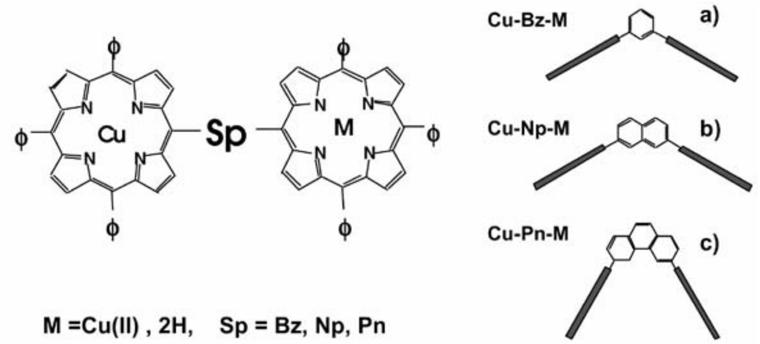


FIGURE 1 Structure of the porphyrin dimers. Bz, Np, Pn abbreviate the benzene, naphthalene and phenanthrene spacer units, respectively.

ligand units. While dipole-dipole interaction is dominated mainly by the distance of the two paramagnetic species as well as by their electron/spin distribution, exchange interaction varies from molecule to molecule. Even though the distances of the two spin centres are identical between molecular systems, it is often observed that the magnitudes of exchange coupling are different by three to four orders. Since the exchange interaction is isotropic, its contribution on the magnetic properties of the whole assemblies is expected to be largely different from that of anisotropic dipole-dipole interaction. However, in general, it is not easy to separate contribution of exchange interaction from that of dipole-dipole interaction in spin-spin coupling, especially in the case that interaction between the two centres is relatively weak, and that the dipole-dipole and exchange couplings are in a similar order of the magnitude.

Metalloporphyrin dimers in which two halves are linked via a rigid spacer are attractive compounds to study spin-spin coupling by varying distance and orientations of the two metal spin centres systematically[1]. Moreover, there is another advantage that we can keep the environment of the paramagnetic metal ion almost identical with changes of the spacer molecule[2, 3].

It is well known that copper(II) porphyrin exhibits complicated hyperfine (hf) structure in its EPR spectrum due to four nitrogen and copper nuclei[4]. When two copper porphyrins constitute a dimer, however, such hf patterns are expected to be deviated by spin-spin coupling of a wide range from several to hundreds gauss. In this work, EPR spectra of three di-copper porphyrin dimers in Figure 1 are presented as well as those of the corresponding copper-free base porphyrin dimers. Analysis and comparison between the spectra obtained in fluid and rigid media leads to provide a direct evidence of weak exchange interaction and allows us to discuss its spacer dependence.

EXPERIMENTAL RESULTS

EPR Spectra in Toluene Rigid Glass at 77 K

Figure 2 shows cw-EPR spectra of TPPCu (monomer), Cu-Pn-H_2, Cu-Pn-Cu measured in toluene rigid glass at 77 K. As can be seen, the EPR spectrum of Cu-Pn-H_2 is coincident with that of the monomer. The same results were obtained for the other two mono-copper dimers. On the other hand, di-copper porphyrin dimers show significant differences in their hf structure, especially in the high magnetic field region. The hf patterns in the three copper porphyrin dimers depend on the spacer and Cu-Bz-Cu exhibits the most unresolved feature.

It is clear that the observed difference of the EPR spectra in the di-copper porphyrin dimers from that of the mono-copper versions is due to spin-spin coupling between the two coppers, but not due to structural changes in dimer formation.

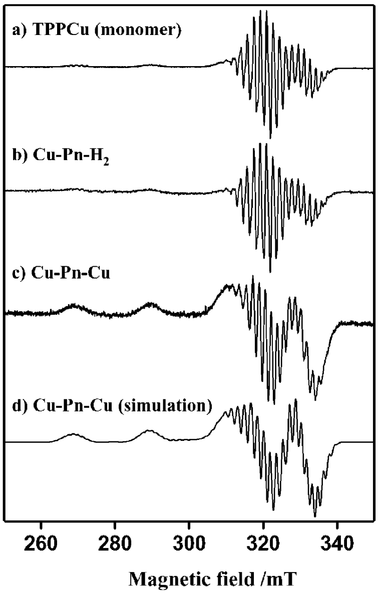


FIGURE 2 X-band cw-EPR spectra in toluene rigid glass at 77 K. a) copper porphyrin monomer, b) mono-copper(II) porphyrin dimer, Cu-Pn-H_2 c) di-copper(II) dimer, Cu-Pn-Cu and d) simulation of the Cu-Pn-Cu spectrum.

EPR Spectra in Toluene Fluid Solution at 300 K

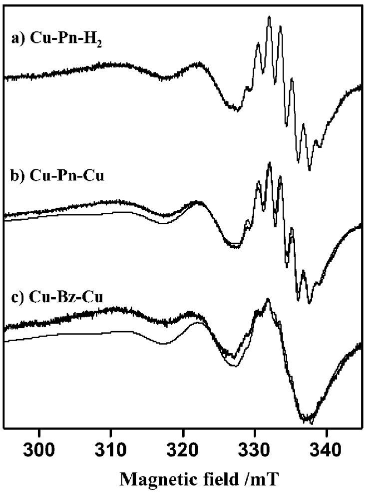


FIGURE 3 X-band cw-EPR spectra in toluene fluid solution at 300 K. a) mono-copper(II) porphyrin dimer, Cu-Pn-H$_2$ b) di-copper(II) porphyrin dimer, Cu-Pn-Cu and c)Cu-Bz-Cu. The solid lines are experimental results whereas the dotted lines are simulations.

Figure 3 shows cw-EPR spectra in toluene solution at 300 K. Note that the total magnetic field width is different from that in Figure 2. In fluid solution, the anisotropy in hf constants and g-factors is averaged for all orientations due to molecular tumbling effect, and thus the total spectral region is narrower than that in the rigid media[5]. This effect also averages out dipole-dipole coupling because of its anisotropy.

A striking result we can see in Figure 3(a),(b) is that there is no remarkable difference between Cu-Pn-H$_2$ and Cu-Pn-Cu in spite of the fact that those two exhibit considerably different spectra in rigid glass at 77K (Figure 2). This implies that exchange coupling in Cu-Pn-Cu is fairly small compared to the hf couplings. The difference between Cu-Pn-H$_2$ and Cu-Pn-Cu at 77 K is attributable to dipole-dipole coupling in Cu-Pn-Cu.

In contrast to the Pn-linked dimers, the EPR spectrum of Cu-Bz-Cu at 300 K (Figure 3(c)) shows considerably broad feature in its hf pattern. Since the mono-copper version of this dimer exhibits essentially the same spectrum as that of Cu-Pn-H$_2$ also in fluid solution, the molecular rotational diffusion rate, which contributes line broadening effectively, should be in the same order of the magnitude between Bz- and Pn-linked dimers. Thus the observed unresolved feature in Cu-Bz-Cu can be concluded due to exchange interaction between the two copper spins.

SIMULATIONS AND DISCUSSION

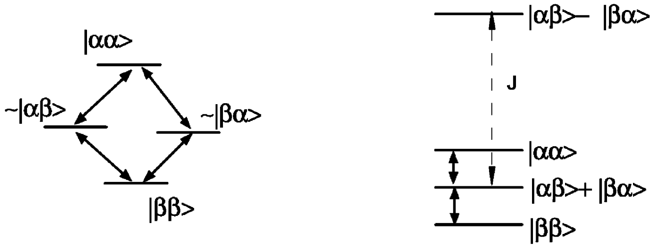
Spin Hamiltonian for a coupled doublet-doublet system is given by

$$H = \omega_A \cdot \mathbf{S}_A + \omega_B \cdot \mathbf{S}_B - J(1/2 + 2 \cdot \mathbf{S}_A \cdot \mathbf{S}_B) + \mathbf{S}_A \cdot \mathbf{D} \cdot \mathbf{S}_B \qquad (1)$$

where ω_i is a resonance frequency of an individual spin, A or B, including hf interactions and given by $\omega_i = g\beta_e \mathbf{B} + \sum_j \mathbf{A}_j \mathbf{I}_j$. The exchange coupling is written as J whereas **D** is a dipolar coupling tensor. When the two spins are coupled weakly, the eigenstates of the system is not separated into singlet and triplet states of the strong coupling condition, but is close to doublet-doublet product states as illustrated in Figure 4.

One of the important differences in the EPR transition lines between fluid and rigid media is that the orientation dependence disappears due to molecular rotational motion in solution[5]. Thus, we can neglect the dipole-dipole coupling term in Eq. 1 under the fluid condition. From simulations for the solution data, where we took into account of a line width depending upon the nucleus spin quantum numbers, exchange coupling for Cu-Pn-Cu and Cu-Np-Cu is found to be $|J| < 10^{-4}$ cm^{-1} whereas that of Cu-Bz-Cu is $4 < |J| < 30 \times 10^{-4}$ cm^{-1}.

On the other hand, dipolar coupling constants in rigid media can be estimated from the distance between the two spin centres. The EPR spectra are well reproduced by taking account of both exchange



(a) weak coupling limit (b) strong coupling limit

FIGURE 4 Schematic diagrams of the coupled doublet-doublet system in the extreme of a) weak coupling and b) strong coupling cases. Arrows in solid line represent EPR transitions.

and dipolar couplings. The exchange coupling, | J |, is evaluated as 2×10^{-4}, 3×10^{-4}, and 20×10^{-4} cm^{-1} for the Pn, Np and Bz bridged copper porphyrin dimers, respectively.

It is noted that although the centre-to-centre distance is almost identical between Pn and Bz bridged dimers, the magnitude of exchange interaction in Cu-Bz-Cu is ten times larger than that of Cu-Pn-Cu. In other words, the centre-to-centre distances in the three dimers are in the order of Pn ~ Bz << Np [2], whereas number of bonds in the spacer unit is Bz < Np < Pn, which seems to be in a good correlation with the obtained | J | values. This observation leads to suggest that through bond mechanism is dominant in exchange interaction of such kind of gable-type porphyrin dimer systems.

CONCLUSIONS

Since the solution spectra have broader line-widths due to the molecular rotational diffusion compared to the solid, it may be more difficult to determine J values. However, the line shape of the solution spectra is not subjected to dipole-dipole interaction under our condition, it provided a strong support for the | J | values evaluated in rigid media as well as their relation among the three compounds. Although the size of | J | is quite small in all three dimers, it is evident that the exchange coupling does not depend on the centre-to-centre distance very much but rather depend on the pathway length which connects to the two halves.

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