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An ESR Study of the Interaction of Copper(II) Octaethylporphyrin with π Acceptors

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The π-π interaction of octaethylporphyrincopper(II) (Cu(OEP)) with π acceptors has been investigated in solution and in magnetically-diluted crystals by ESR, and the perpendicular components of the ESR parameters for Cu(OEP) in various states have also been determined with considerable accuracy. It has been revealed that, upon the formation of charge-transfer complexes between Cu(OEP) and π acceptors, the *g* values decrease slightly, the copper hyperfine coupling constants remain almost unchanged, and the absolute values of the nitrogen superhyperfine coupling constants increase slightly. Accompanying changes in the electronic structure around the copper ion have been discussed. The ESR parameters of Cu(OEP) doped in Ni(OEP) have been noted to depend significantly upon the polymorphism of the diluent.

The dimerization and/or aggregation of planar metal complexes with π-ligands are phenomena in which the π-π interaction between the metal complexes plays an important role.[1-5] The π-π interaction of metal complexes with π acceptors or donors, which results in the formation of charge-transfer (CT) complexes in some cases, is also a subject of study aimed at elucidating the electron-transfer mechanisms, both in co-ordination chemistry and in biochemistry.[6,7] The CT complexes between metal porphyrins and various π acceptors are the best studied group.[8-10] Little work, however, has been done to investigate how the electronic structure of the metal complexes changes in the CT complexes. In the present work, such an attempt for a copper(II) porphyrin has been made by means of the ESR method.

In ESR studies of copper(II) porphyrins, we must know that it is not easy to determine precisely the perpendicular components of copper ESR parameters from the ESR spectra of frozen solutions and magnetically-diluted polycrystals. The usual computer-simulation method is not always useful for this purpose, since none of the simulated spectra thus far obtained for the systems have been fitted to the observed ones with any considerable accuracy.[11-14] This situation can further be understood from the fact that the $g_\perp$ and $|A_\perp|$ values previously reported for the copper(II) complexes of porphyrins and phthalocyanine are randomly distributed over the wide ranges of 2.031—2.072 and 0—54×10^{-4} cm^{-1} respectively.[11-18] In this work, those parameter values of octaethylporphyrincopper(II) in various states have been estimated on reasonable grounds.

Experimental

Materials. Octaethylporphyrin (abbreviated as OEPH$_2$) was obtained from the Stern Chemical Co., and its Cu(II) and Ni(II) complexes (Cu(OEP) and Ni(OEP) respectively) were prepared and purified according to the literature.[19] 1,3,5-Trinitrobenzene (TNB), 2,4,7-trinitrofluoren-9-one (TNF), piperidine (pip), and toluene were purchased from the Tokyo Kasei Co. and were purified by the standard literature methods. Doped samples were obtained by crystallization from 200: 1 mixtures of the diamagnetic matrix substance and the substituent one in dichloromethane and in *N,N*-dimethylformamide (DMF). The 1: 1 CT complexes of M(OEP)·TNF and OEPH$_2$·TNF were deposited as black needles immediately after the addition of an equimolar TNF to the dichloromethane solutions of M(OEP) and OEPH$_2$; the CT complexes were confirmed by elemental analyses. The sample of Cu(OEP) doped in Ni(OEP) will hereinafter be abbreviated as Cu/Ni(OEP); similar abbreviations will also be used for the other doped samples.

Physical Measurements. The ESR spectra at room temperature for both polycrystalline and solution samples and at 77 K for frozen solutions were recorded on a Varian E-4 X-band ESR spectrometer, the field strength being calibrated with an NMR probe and then with bis(2,4-pentanedionato)oxovanadium(IV) in benzene. The visible absorption spectra at room temperature were recorded on a Cary 14 spectrophotometer.

Results

The ESR spectrum of Cu(OEP) in toluene at 77 K is shown in Fig. 1(A). The undulation of the base-line, on which the monomer spectrum is superimposed, indicates the co-existence of triplet-state dimers; this was further evidenced by the half-field spectrum clearly observed around 1550 G.† The dimerization and/or polymerization of metal porphyrins in solution have been extensively studied by ESR[12,13,20-22] and by the other methods.[3-5] Their dimerization ability itself suggests that their molecules have the property

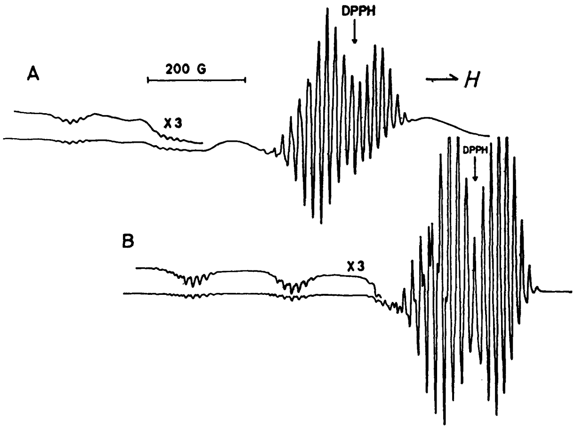

Fig. 1. X-Band ESR spectra of Cu(OEP) in toluene at 77 K.
(A) Without and (B) with an excess of TNB ([TNB]/[Cu(OEP)]=30).

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† 1 G=10^{-4} T.

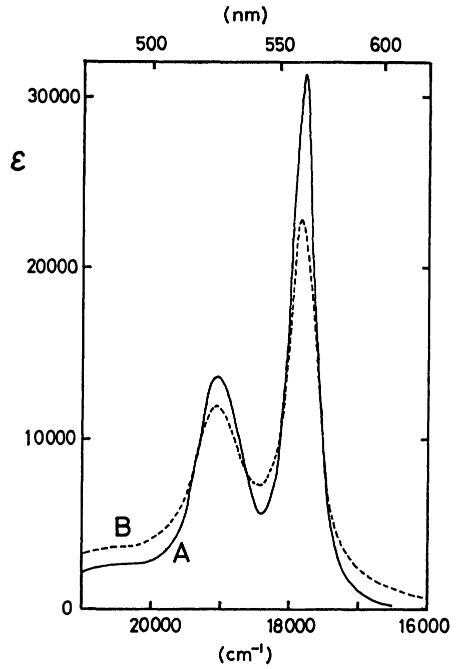

Fig. 2. Visible absorption spectra of Cu(OEP) in toluene at room temperature.
(A) and (B) correspond to those in Fig. 1 respectively.

of interacting readily with other π-systems. The frozen solution ESR spectrum of Cu(OEP) in toluene with excess TNB is shown in Fig. 1(B). This spectrum, in which dimer ESR signals disappear completely, is comparatively sharp in every absorption line. On the other hand, the visible absorption spectra of Cu(OEP) in toluene with and without excess TNB are as shown in Fig. 2. The spectral change on the addition of excess TNB is quite similar to that in the case of Co(OEP),[8] in which the 1: 1 CT complex formation of Co(OEP)·TNB has been confirmed.

The ESR parameters determined directly and definitely from such ESR spectra as are shown in Fig. 1 number only three or four, $g_{//}$, $|A_{//}|$, $|A^N_{\perp}|$, and, possibly, $|A^N_{//}|$.[22] As has already been mentioned, the exact determination of the perpendicular components of g and A is not easy at present. Toluene is generally considered as an inert or non-co-ordinating solvent, and Cu(OEP) is a very stable square-planar complex with strong co-ordination bondings. In such a case, the relations of $g_0=(g_{//}+2g_{\perp})/3$ and $A_0=(A_{//}+2A_{\perp})/3$ hold well, where g_0 and A_0 are the parameters derived from fluid-solution ESR spectra and where the other parameters are those from their frozen-solution ESR spectra.[24] In Fig. 3, the observed ESR spectrum of Cu(OEP) in toluene at room temperature is shown, together with the simulated one, in which isotope effects due to the natural occurrence of ^{63}Cu and ^{65}Cu, a second-order correction of the resonance fields, and Lorentzian line shapes with M_I-dependent linewidths are taken into consideration.[25] The same simulation was done for the toluene solution of Cu(OEP) and excess TNB. The $g_{\perp}$ and $|A_{\perp}|$ values of both spectra shown in Fig. 1 were thus determined with a certain degree of reliability. The $g_{\perp}$ and $|A_{\perp}|$ values of the other frozen-solution type of spectra were obtained by a direct comparison between their spectra and the spectra shown in Fig. 1 in the perpendicular region. Some representative polycry-

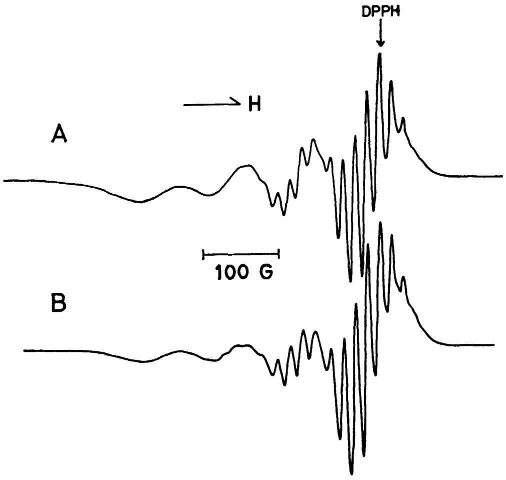

Fig. 3. X-Band ESR spectra of Cu(OPE) in toluene at room temperature.
(A), Observed; (B), simulated with $g_0=2.094$, $|A_0|=86.4$ G, $|A^N{}_0|=16.0$ G, and 3.5, 5.2, 6.9, and 8.7 G for the line widths of $M_I=3/2$, 1/2, $-1/2$, and $-3/2$ lines, respectively.

Table 1. ESR parameters[a)] for Cu(OEP) in various states

Complex	Solvent or matrix	$g_{//}$	$g_{\perp}$	g_0	$10^3\|A_{//}\|$ (cm^{-1})	$10^3\|A_{\perp}\|$ (cm^{-1})	$10^3\|A_0\|$ (cm^{-1})	$10^3\|A^N_{\perp}\|$ (cm^{-1})	$10^3\|A^N_{//}\|$ (cm^{-1})	$10^3\|A^N_0\|$ (cm^{-1})
Cu(OEP)	Toluene	2.187	2.047	2.094	20.4	2.4	8.4	1.45	1.83	1.57
Cu(OEP)·TNB	Toluene	2.181	2.045	2.092	20.4	2.5	8.5	1.46	1.85	1.58
Cu(OEP)·pip	Toluene	2.215	2.058		18.9			1.37	1.68	
Cu(OEP)	OEPH$_2$	2.190	2.048		19.8	2.3		1.43	1.70	
Cu(OEP)·TNF	OEPH$_2$·TNF	2.186	2.047		19.9	2.4		1.44	1.71	
Cu(OEP)[b)]	Ni(OEP) (I)	2.190	2.049		19.9	2.3		1.46	1.75	
	Ni(OEP) (II)	2.175	2.044		20.2	2.5		1.49	1.75	
Cu(OEP)·TNF	Ni(OEP)·TNF	2.186	2.047		20.0	2.4		1.47	1.76	

a) All the values of copper hyperfine are given for ^{63}Cu. The estimated errors are ± 0.001 for g, $\pm 0.1\times 10^{-3}$ cm^{-1} for A, and $\pm 0.01\times 10^{-3}$ cm^{-1} for A^N, but the respective relative errors among related complexes cited for comparison are less. All the A^N values were determined from partially enlarged spectra. b) (I), Crystallized from DMF; (II), crystallized from dichloromethane. All the other crystalline complexes were obtained by crystallization from dichloromethane.

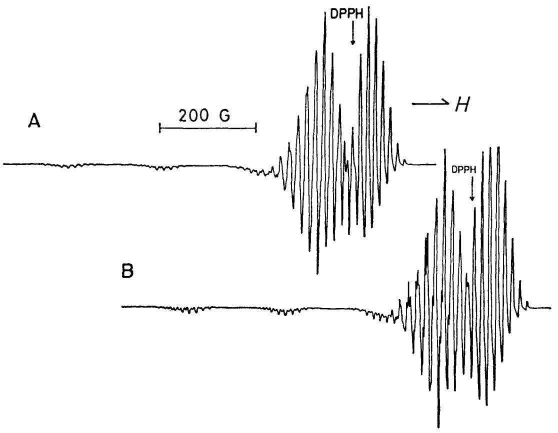

Fig. 4. X-Band polycrystalline powder ESR spectra of (A) Cu(OEP)/OEPH$_2$ and (B) Cu(OEP)·TNF/OEPH$_2$·TNF at room temperature.

stalline ESR spectra are shown in Fig. 4, just for information. All the ESR data thus determined are summarized in Table 1. The $g_\perp$ and $|A_\perp|$ values listed in the table agree well with those recently reported for copper(II) ^{15}N-etioporphyrin I in the free base.[18] This confirms the values in Table 1 to be reliable.

Discussion

Piperidine, which is a basic and saturated molecule with a nitrogen lone-pair, can co-ordinate apically to copper(II) porphyrins to form square-pyramidal five-co-ordinate complexes.[26] The ESR parameters change remarkably on the addition of piperidine to the toluene solution of Cu(OEP), as is shown in Table 1; the g and $|A|$ values remarkably increase and decrease respectively. These types of ESR changes for planar copper(II) complexes are generally caused by a change in the state of apical co-ordination.[27–29]

On the other hand, on the addition of an excess of TNB to the toluene solution of Cu(OEP), the ESR parameters changed, too, but in a different way; the g values decreased slightly, the $A_{/\!/}$ value remained almost unchanged, and the $|A^N|$ values increased slightly. These facts show that piperidine and TNB have quite different types of interaction with Cu(OEP). A closer inspection of the table indicates that there are similar ESR changes in the crystalline states, too. In the case of Cu/Ni(OEP), however, (I) rather than (II) is adopted for comparison; this point will be discussed later. The same kind of ESR results for another complex in crystals can be found in the literature:[30] $g_{/\!/}=2.212$, 2.206, and 2.206, and $10^3|A_{/\!/}|=$ 19.98, 19.91, and 20.15 (cm^{-1}), for Cu/PdOx$_2$, Cu/PdOx$_2$·2TCNE, and Cu/PdOx$_2$·TCNQ respectively, where Ox, TCNE, and TCNQ are the abbreviations of 8-quinolinate, tetracyanoethylene, and 7,7,8,8-tetracyanoquinodimethane respectively. These data, however, have been discussed only from the point of view of a general understanding of host-lattice effects.

As to the host-lattice effects, it is interestingly found in Table 1 thai the polycrystals of Cu/Ni(OEP) obtained by crystallization from DMF, (I), are remarkably different in ESR parameters from those crystallized from dichloromethane, (II). The difference is not the kind of difference which can be explained in terms of a change in the state of apical co-ordination. Ni(OEP) is well known to display polymorphism.[31,32] Two crystalline modifications with known X-ray analytical data have quite different molecular geometries and packings, although the complex is naturally very stable. Judging from the essence of polymorphism, however, the difference in energy between the crystalline modifications must not be large. The above-mentioned ESR result of Cu/Ni(OEP) shows that molecular-environmental effects due to polymorphism are sensitively reflected in the ESR parameters. It is noteworhy that the structure and properties of metal porphyrins depend to a marked extent on their molecular environment, and this seems to be of especial significance in view of the functional diversity of the complexes in biological systems. In Table 1, Cu(OEP)/OEPH$_2$ and (I) in Cu/Ni(OEP) have almost the same ESR parameters. This fact suggests that they are crystallographically similar, although the solvents of crystallization are different. In this study, accordingly, (I) in Cu/Ni(OEP), rather than (II), was adopted to compare with Cu/Ni(OEP)·TNF.

On the whole, it may be concluded that, when Cu(OEP) interacts with π acceptors, the g values decrease slightly and the $A_{/\!/}$ value remains almost unchanged. In an axial molecular field, the σ antibonding wavefunction is:[33,34]

$$\phi_\sigma = \alpha d_{x^2-y^2} - (\alpha'/2)(\sigma_1-\sigma_2+\sigma_3-\sigma_4)$$
$$\alpha^2 + \alpha'^2 - 2\alpha\alpha' S = 1$$

where σ_i expresses the ith nitrogen lone-pair orbital and where the other symbols have their usual meanings. The bonding parameter, α, is a measure of the covalency of the in-plane σ bonding. To calculate α^2, an approximate formula based on the copper hyperfine term, $A_{/\!/}$, can be used:[35]

$$\alpha^2 = -(A_{/\!/}/P) + (g_{/\!/}-2) + (3/7)(g_\perp-2) + C$$

where C is a small constant and where $P=2\gamma\beta_0\beta_n \langle r^{-3}\rangle=0.0360$ cm^{-1}. According to this equation, the ESR changes mentioned above obviously lead to a slight decrease in value of α^2. The decrements ($\Delta\alpha^2$) are calculated to be -0.003—-0.008, meaning that the σ bonding becomes a little more covalent when Cu(OEP) interacts with π acceptors. This result is also supported by the experimental fact that both $|A_\perp^N|$ and $|A_{/\!/}^N|$ values simultaneously increase slightly, as is shown in Table 1. The increments of $|A^N|$ are of a reasonable order of magnitude, in view of the relations of $\Delta\alpha'^2 \simeq -\Delta\alpha^2$ and the rough proportionality between $\Delta\alpha'^2$ and $\Delta|A^N|$.[34] This suggests that either of two changes in the electronic structure of Cu(OEP) may take place on the formation of its CT π-complexes. One of the changes is that the π-electron density at the four co-ordinating nitrogen atoms slightly increases in order for the σ co-ordination bonding to become a little more covalent.[24] The other change is that the electronic charge on the central copper atom increases slightly relatively in the CT complexes, so that the copper $d_{x^2-y^2}$ orbital level is lowered and, accordingly, the orbital becomes easier to be mixed with the ligand σ orbitals.[36,37] These considerations do not seem unreasonable, since a small change in the distribution of π-electrons over the whole Cu(OEP) molecule must actually take place on the formation of its CT π-complexes. Further work will, however, be required to find a solution to this problem.

It is interesting to consider the differences between (I) and (II) in Cu/Ni(OEP) in Table 1, for instance, as to the value of α^2. If we assume $\alpha^2=0.803$ for (I),[25] the α^2 value of (II) can be calculated to be 0.794 from the above-described equation of α^2. This change in α^2, which is a host-lattice effect, is large compared with that in the CT complexes. This fact shows the importance of lattice effects or molecular environmental effects on the properties of metal prophyrins.

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$$\begin{aligned}\mathscr{H}= \beta_0[{}^{//}gH_zS_z+g_\perp(H_xS_x+H_yS_y)] &+ A_{//}S_zI_z \\ + A_\perp(S_xI_x+S_yI_y) &+ S_x[A^N_{//}(I_{1x}+I_{3x})+A^N_\perp(I_{2x}+I_{4x})] \\ &+ S_y[A^N_\perp(I_{1x}+I_{3x})+A^N_{//}(I_{2y}+I_{4y})] \\ &+ S_z[A^N_\perp(I_{1z}+I_{2z}+I_{3z}+I_{4z})]\end{aligned}$$

where the four ligand nitrogen atoms on the xy plane are numbered 1 to 4.

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