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An ESR Study of 5-Formazanyl Copper(II) Complexes as an Analogy to Three Types of Copper-Containing Proteins

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The Electron Spin Resonance(ESR) spectra of ten 5-formazanyl copper(II) complexes in toluene solutions have been observed at room temperature and at that of liquidnitrogen. The ESR($g_{/\!/}$ and $A_{/\!/}$) and bonding(α^2) parameters of the copper ion were greatly affected by substituting several groups at the ortho position of 1-phenyl ring of formazan. Based on these results, the complexes are classified into three groups: Group I, in which $A_{/\!/}\approx 0.012$—$0.013\,\mathrm{cm}^{-1}$ and $\alpha^2\simeq 0.5$; Group II, in which $A_{/\!/}\approx 0.017\,\mathrm{cm}^{-1}$ and $\alpha^2\simeq 0.7$, and Group III, in which two copper ions are interacting. It is clarified that they correspond nicely to three types of copper-containing proteins previously investigated.

Since Kuhn and Jerchel studied the tetrazolium salts of formazan in a program of research on invert soap,[1] these compounds, with their remarkable biological potentialities, have been extensively investigated. Especially, formazans obtained by the reduction of the corresponding tetrazolium salts have been widely utilized to check enzyme activity in plant and animal tissues.[2]

Formazans have been known to form complexes with some transition metals having the stoichiometries of 2:1 and 1:1.[3–5] Previously, we ourselves reported that some copper complexes of formazan show small isotropic splitting constants of the copper ion in the ESR spectra of these complexes and that their magnetic properties change drastically with different kinds of substituents to the 1-phenyl ring of 1,3,5-triphenyl-5-formazan (Fig. 1).[6] These results have motivated us to undertake a thorough examination of the substituent effects on the electronic states and magnetic properties of these complexes.

Many studies of copper complexes have established that the structural configuration around the copper ion is affected by the inductive property of the substituent group,[7,8] the distortion due to the bulky substituents,[9,10] and the apical coordination of the solvent molecules, in addition to the symmetry of the ligand field.[11,12] The change in the ESR parameters has been discussed in relation to various kinds of binding sites of copper proteins. A comparison of ESR data of the binding sites of copper proteins with those of well-defined model complexes enables us to suppose micro-structural information about the area around the copper ion in proteins.[13–17] Thus, the copper ions in the various copper proteins thus far investigated have been classified into three types, based on ESR spectroscopic studies.[18–21]

The effects of the substituent groups on the copper complexes mentioned above have thus far been found in the range of a perturbation within each type of copper-containing protein. However, we have now found that the copper-ion environment in 5-formazanyl copper(II) complexes is much affected by the introduction of different substituent groups into formazan and that the change in the spectroscopic behavior due to these substituents extends over all three types. Therefore, we have attempted to establish the micro-structural details of the present complexes and the analogy to the binding site of copper-containing proteins.

In this paper, we will report the results of our ESR spectroscopic study of copper complexes of formazan with several kinds of substituents. The results obtained are examined based on the inductive, distortional, and coordinational effects. Finally, the configulational change suggested by the ESR and bonding parameters will be discussed in relation to three types of copper-containing proteins.

Experimental

Preparation of Samples. 1,3,5-Triphenyl-5-formazan, which has no substituent in the 1-phenyl ring, is shown in Fig. 1. Formazans with a para or ortho substituent in the 1-phenyl ring were obtained by the reaction of the diazonium salts of para- or ortho-substituted aniline with benzaldehyde phenylhydrazone by a method described elsewhere.[22] (Hereafter, we will abbreviate the substituent as X.) The copper complex was prepared by mixing ethanol solutions of formazan and copper acetate monohydrate.[4] The precipitate was obtained by the addition of water to the ethanol solution. Recrystallization was also carried out in the ethanol solution. The complexes obtained consisted of a fine powder and so could not be submitted to X-ray crystallographic measurements. The analytical data of the complexes prepared for the present study are listed in Table 1. The complexes obtained are abbreviated as *p*-X-Cu (2:1) for bis[1-(*p*-X phenyl)-3,5-diphenyl-5-formazanyl]copper and *o*-X-Cu (1:1) for bis[1-(*o*-X phenyl)-3,5-diphenyl-5-formazanyl]dicopper.

Physical Measurements. The X-band (9 GHz) ESR spectra were obtained in the toluene solutions of the

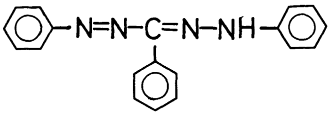


Fig. 1. 1,3,5-Triphenyl-5-formazan.

Table 1. Analytical Data of the 5-Formazanyl Copper(II) Complexes

Complex	Molecular formula	Found(%)				Calcd(%)			
		C	H	N	Halogen	C	H	N	Halogen
1, *p*-H-Cu(2:1)	$C_{38}N_8H_{30}Cu$	68.8	4.6	16.6		68.9	4.5	16.4	
2, *p*-Cl-Cu(2:1)	$C_{38}N_8H_{28}Cl_2Cu$	61.7	3.9	14.8	9.9	62.4	3.9	15.3	9.7
3, *p*-Br-Cu(2:1)	$C_{38}N_8H_{28}Br_2Cu$	55.6	3.4	13.5	19.3	55.7	3.4	13.7	19.5
4, *p*-NO$_2$-Cu(2:1)	$C_{38}N_{10}O_4H_{28}Cu$	60.5	3.7	18.6		60.7	3.7	18.6	
5, *p*-CH$_3$-Cu(2:1)	$C_{40}N_8H_{34}Cu$	70.0	4.9	15.2		69.6	4.9	16.2	
6, *o*-CH$_3$-Cu(2:1)	$C_{40}N_8H_{34}Cu$	69.7	4.9	16.2		69.6	4.9	16.2	
7, *o*-Cl-Cu(2:1)	$C_{38}N_8H_{28}Cl_2Cu$	61.8	3.6	14.1	10.7	62.4	3.9	15.3	9.7
8, *o*-Br-Cu(2:1)	$C_{38}N_8H_{28}Br_2Cu$	55.2	3.4	13.9	19.3	55.7	3.4	13.7	19.5
9, *o*-COOH-Cu(1:1)	$C_{40}N_8O_4H_{28}Cu_2$	59.0	3.6	13.5		59.2	3.5	13.8	
10, *o*-OH-Cu(1:1)	$C_{38}N_8O_2H_{28}Cu_2$	60.6	3.9	14.8		60.4	3.7	14.8	

complex at room temperature and in frozen glasses at 77 K with a JEOL ME-3X spectrometer equipped with 100 KHz field modulation. The Mn^{2+} in MgO was used as a standard sample for the calibration of the magnetic field. The optical spectra of the complexes were measured in toluene solutions at room temperature by the use of a Shimazu Double-beam Spectrophotometer, UV200, in the range of 300—700 nm and by the use of a Shimazu Multi-purpose Spectrophotometer, MPS50L, in the range of 600—2000 nm.

Results

The 5-formazanyl copper complexes obtained are classified into two categories on the basis of the stoichiometry of formazan and the copper ion from the results of the elemental analyses; one is of a 2:1 stoichiometry of formazan and the copper ion, while the other is of 1:1. Based on the ESR parameters to be described below, the former is further divided into two groups, Group I and Group II; the latter is abbreviated as Group III. The molecular structures of the complexes tentatively suggested by the elemental analyses are shown in Fig. 2(a) for the complexes in Groups I and II and in Fig. 2(b) for those in Group III. The latter shows the dimer structures of the complex. The complexes belonging to each group are listed in Table 2.

Group I. The ESR spectrum of *p*-H-Cu (2:1), **1**, in a toluene solution at room temperature is shown in Fig. 3(a) as a typical example of the spectra of the complexes belonging to Group I. The spectra of the complexes of Group I consisted of four ill-resolved resonance lines attributable to one copper ion (I=3/2). In some complexes, further splittings around 0.0005 cm^{-1} were observed at the absorption line in the highest field; they were unambiguously assigned to the superhyperfine interaction between the unpaired electron of the copper ion and the ligand-nitrogen nuclei. The isotropic copper splitting constants, A_{iso}(Cu), are around 0.004 cm^{-1}. These values are extremely small compared with those of the ordinary copper complexes with a planar configuration.[23,24)

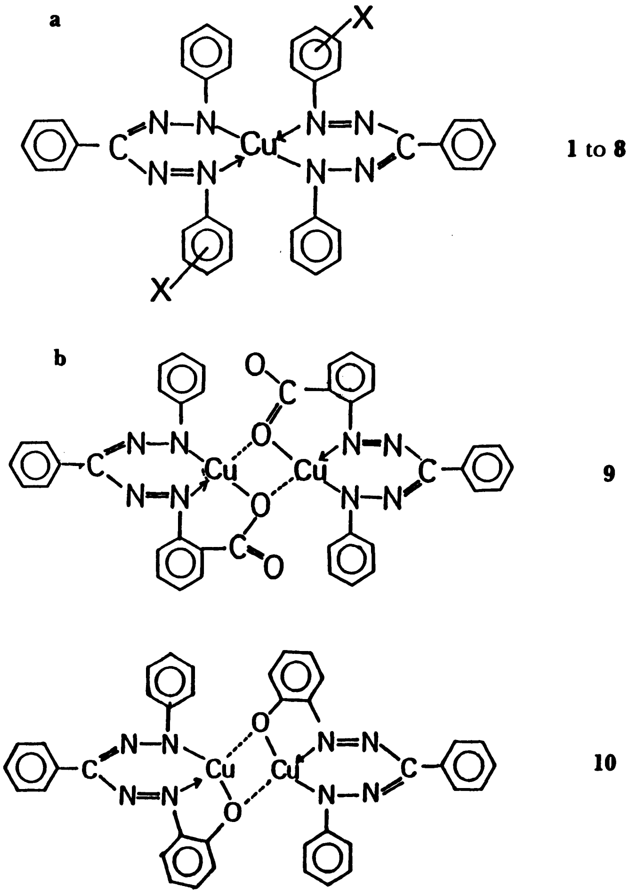


Fig. 2. **a**, Bis[1-(*p*-X phenyl)-3,5-diphenyl-5-formazanyl]copper, **1**: X=H; **2**: X=Cl; **3**: X=Br; **4**: X=NO$_2$; **5**: X=CH$_3$. Bis[1-(*o*-X phenyl)-3,5-diphenyl-5-formazanyl]copper, **6**: X=CH$_3$; **7**: X=Cl; **8**: X=Br. **b**, **9**, Bis[1-(*o*-carboxyphenyl)-3,5-diphenyl-5-formazanyl]-dicopper, and **10**, bis[1-(*o*-hydroxy)-3,5-diphenyl-5-formazanyl]dicopper.

The ESR spectrum of **1** obtained in a frozen toluene solution at 77 K is shown in Fig. 3(b), which is also typical of monomeric copper species. The g values, g_1, g_2, and g_3, which were experimentally determined in the ESR spectra at 77 K, are tabulated in Table 2. The g_1 clearly corresponds to the usual notation, $g_{/\!/}$.

Table 2. ESR and Bonding Parameters, and Visible Absorptions of *p*-X-Cu and *o*-X-Cu in Toluene

Complex	g_1	g_2	g_3	g_{ave}	A_1(Cu)	A_2	A_3	A_{iso}(Cu)	α^2	Absorption maxima
					10^{-4} cm^{-1}					nm
1, *p*-H-Cu	2.114	2.032	1.991	2.043	115	8.5	—	38	0.47	440, 470(sh)a), 590, 790
2, *p*-Cl-Cu	2.115	2.034	1.984	2.045	121	6.5	—	38	0.49	440, 580, 780
3, *p*-Br-Cu	2.113	2.032	1.985	2.044	120	7.9	8.2	38	0.49	450. 590, 780
4, *p*-NO_2-Cu	2.111	2.031	1.985	2.043	121	5.6	—	38	0.49	480, 600, 780
5, *p*-CH_3-Cu	2.121	2.032	1.984	2.046	120	7.4	—	38	0.49	440, 560, 800
6, *o*-CH_3-Cu	2.122	2.035	1.983	2.049	132	6.9	—	41	0.55	420, 500, 540, 750
7, *o*-Cl-Cu	2.120	2.031	1.991	2.048	169	15.4	15.4	77	0.60	485, 590
8, *o*-Br-Cu	2.125	2.019		2.054	175	16.5		77	0.63	485, 590
9, *o*-COOH-Cu	2.192	2.054	1.986	2.077	163	18.5	—	65	0.69	555, 580(sh), 820
10, *o*-OH-Cu	2.143	2.026	1.978	2.049	179	16.0	18.6	71	0.68	580, 820

a) "sh" designates shoulder.

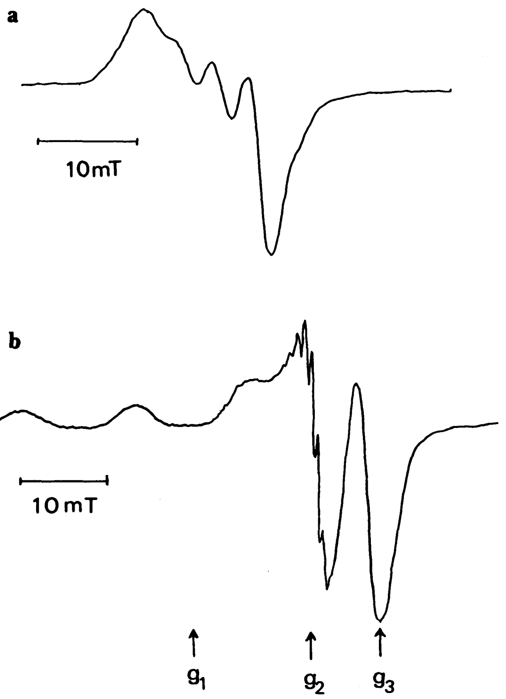


Fig. 3. ESR spectra of **1** in toluene solution at (a) room temperature and (b) liquid-nitrogen temperature. Further splittings were not observed in (a).

The g_2 and g_3 can not, however, be uniquely assigned to g_x and g_y. The splitting of 0.012 cm^{-1} at the g_1 position, A_1(Cu), can reasonably be assigned to the parallel component of the copper hyperfine splittings, $A_{//}$(Cu). This value is also small compared with those of the usual planar copper complexes. Further splitting constants at the g_2 and g_3 positions are represented as A_2 and A_3 respectively. These can not be uniquely assigned to the splittings due to the *x* and *y* components of the copper ion, for the splittings due to the four equivalent nitrogen nuclei may overlap. However, in view of the apparent intensity ratios of the absorption lines at the g_2 and g_3 positions, the assignment of these splittings to the ligand nitrogens seems most plausible. The ESR parameters of the other complexes of Group I, **2**, to **6**, are also tabulated in Table 2. These parameters of Group I are almost all the same in spite of the various kinds of substituents.

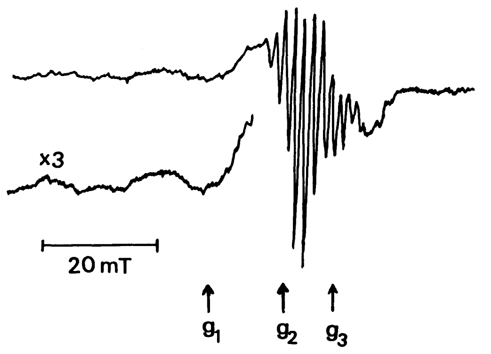


Fig. 4. ESR spectrum of **7** in toluene solution at liquid-nitrogen temperature.

Group II. Figure 4 shows the ESR spectrum of *o*-Cl-Cu (2:1), **7**, in a toluene solution at 77 K. The ESR spectral patterns of this complex at room temperature and 77 K were similar with those of Group I except for the fact of the larger values of A_1(Cu), A_2, A_3, and A_{iso}(Cu). A_1(Cu) and A_{iso}(Cu) are 0.017 cm^{-1} and 0.0077 cm^{-1} respectively. A_2 and A_3 are 0.0015 cm^{-1}. These are usual values in copper complexes with planar or pseudo-planar configurations.23,24) Their *g* values are also similar to those of the complexes of Group I. In the ESR spectrum of *o*-Br-Cu (2:1), **8**, in a toluene solution at 77 K, the splitting constants of the copper ion and the *g* values are similar with those of **7** except for the property of the axial symmetry with g_2=g_3 and A_2=A_3.

Group III. As has previously been reported, the ESR of *o*-COOH-Cu (1:1), **9**, in a toluene solution showed only one sharp single line and did not reveal any hyperfine structure at either room temperature or

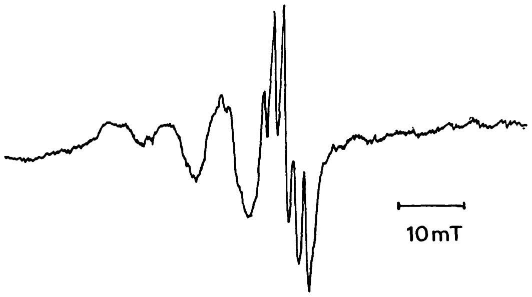


Fig. 5. ESR spectrum of **10** in toluene solution at room temperature. Superhyperfine splittings due to ligand nitrogens are observed in the absorption line at the highest field.

the temperature of liquidnitrogen. The temperature dependence of the magnetic susceptibility of the powdered sample could well be interpreted on the basis of the ground triplet-excited singlet model for the dimeric species of the copper ions.[25] Therefore, one absorption line was attributed to the exchange interaction between two copper ions. In order to get further information about the copper monomer, the addition of pyridine to the toluene solution was attempted. As a result, the hyperfine structure due to the copper monomer appeared at room temperature and that of liquidnitrogen. The data in Table 2 are what were obtained in this way: The $g_{\mathrm{ave}}(\mathrm{Cu})$ of **9** is slightly larger than those of Group II, but $A_{\mathrm{iso}}(\mathrm{Cu})$ and $A_{\mathrm{l}}(\mathrm{Cu})$ are similar to those of Group II. These values of **9** might, by the addition of pyridine, have been varied from those without the solvation of pyridine.[26] However, the visible absorptions did not show any appreciable change by the addition of pyridine. Therefore, it is conceivable that the configurational change around the copper ion may be small in the pyridine-added toluene solution.

The ESR spectrum of *o*-OH-Cu (1:1), **10**, in the toluene solution at room temperature consisted of four lines attributable to the copper monomer (Fig. 5). Further splittings to five lines at the absorption in the highest field provide firm evidence that the two nitrogens of the ligand take part in the superhyperfine interaction. At the temperature of liquidnitrogen the typical spectrum of the usual copper ion with an anisotropy was observed. The ESR parameters of the monomer were similar to those of Group II. In the microcrystalline state, on the other hand, the ESR spectrum of the triplet state was observed at room temperature on both sides of the absorption line attributable to the monomeric species of the copper ion, as is shown in Fig. 6. The absorption line without the asterisk around 0.3 T corresponds to that of the copper monomeric species. The signal intensity of the triplet state became too weak to be recognized at 77 K. It is obvious from these facts that the two copper ions are interacting with each other through exchange interaction. The details of the triplet state, including the estimation of the zero-field-splitting parameter, D, will be reported elsewhere.

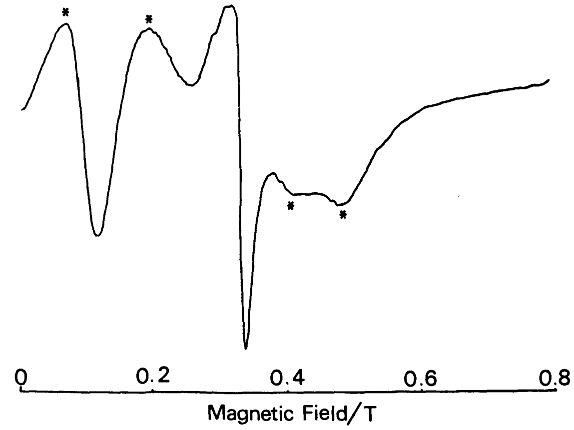


Fig. 6. ESR spectrum of **10** in microcrystalline state at room temperature. The asterisks in the spectrum show the absorptions due to the excited triplet state of the dimer. These disappear at liquid-nitrogen temperature. The central part of the spectrum is due to the monomeric species.

Discussion

Table 2 indicates that the unsubstituted 5-formazanyl copper, **1**, and all of the complexes with para substituent groups, **2** to **6**, belong to Group I. The symmetry around the copper ion in these complexes can plausibly be considered to be planar or pseudo-planar, based upon the g values and the hypothetical molecular structures. On the other hand, the complexes with ortho substituent groups belong to all three groups, suggesting that the substitution results in a different ligand configuration around the copper ion.

The change in the electronic state of the copper ion has been discussed on the basis of: 1) The electron-inductive effect caused by the substituent groups, 2) the distortional effect caused by the substituent groups, and 3) the apical coordination effect, caused mainly by the solvent molecules. The effects of the increased electron-donating ability of the substituent groups on the ESR parameters are to decrease $g_{/\!/}$ and to increase $A_{/\!/}(\mathrm{Cu})$. The ESR behavior of Group I did not depend upon the electron-donating ability of the para substituent groups. The trend of the change in $g_{/\!/}$ and $A_{/\!/}(\mathrm{Cu})$, expected from the increase in the electron-donating ability (–Cl, –Br, –H, and –CH_3), was not observed in the complexes with the ortho substituent groups. Therefore, the electron-inductive effect of the substituent groups is not dominant in the para and ortho substituents. Yokoi et al. reported that the distortional effect becomes dominant when the substituent groups are bulkier.[9] In such a case, $A_{/\!/}(\mathrm{Cu})$ decreases and $g_{/\!/}$ increases with the degree of distortion from the plane containing the copper ion. The facts that *o*-H-Cu (2:1), **1**, and *o*-CH_3-Cu (2:1), **6**, are in Group I, while *o*-Cl-Cu (2:1), **7**, and *o*-Br-Cu (2:1), **8**, are in Group II obviate the importance of the distortional effect caused by the substituent groups on the electronic state of the copper ion. The apical coordination of the solvent molecules is weak in the case of the toluene solution. Therefore, it may be concluded that the three effects mentioned above are not adequate to interpret the drastic change in the ESR parameters shown in Table 2.

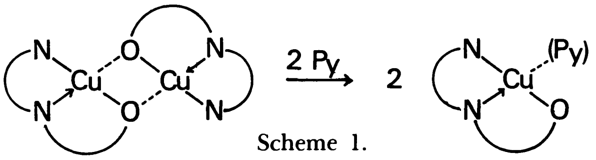
For the probable structure with the square-planar symmetry and with the ground orbital of $d_{x^2-y^2}$,[27] Kivelson and Neiman defined a bonding parameter, α^2.[28] Here we will use α^2 expressed semiempirically by Bryce:[29]

$$\alpha^2 = \frac{A_{/\!/}}{P} + (g_{/\!/} - 2.0023) + \frac{3}{7}(g_{\perp} - 2.0023) + 0.04$$

where P=0.04 cm^{-1}. In order to ascertain the bonding characters of the copper ion under the assumption of the square-planar symmetry around the copper ion, the bonding parameters of Group I and II are compared. In a previous paper, the square-planar structure around the copper ion in the microcrystalline state of **1** was presumably adopted with reference to the g values of the other copper complexes with the square-planar symmetry.[6] Though the three different values of the g component in the frozen toluene solutions of the present complexes suggest a deviation from the square-planar symmetry around the copper ion, the structure is presumed not to be much changed from the planarity, for the difference between g_2 and g_3 is not very large. Under these assumptions, the bonding parameters, α^2, of Group I and II were calculated; they are tabulated in the last column of Table 2.

The deviation from 1.0 shows the degree of covalency of the bonding. The fact that α^2 in Group I, about 0.5, is extremely small indicates the strong covalency in the bonding between the copper ion and the ligands. Such small values have previously been reported with respect to the complexes with sulfur coordination and to plastocyanine, in which the sulfur coordination was determined by means of X-ray analyses.[30,31] On the other hand, the α^2 around 0.7 of Group II is not so small and is comparable to those of Cu-phthalocyanine (0.73) and Cu-tetraphenylporphyrine (0.79).[21] Therefore, it may be concluded that the bonding conditions of Group I and Group II differ considerably.

The toluene solution of **9** showed only a single line, without any hyperfine splitting, at room temperature and at that of liquidnitrogen. These results can be well-interpreted by assuming that, even in a toluene solution, the dimeric structure shown in Fig. 2(b) is retained and that the exchange interaction between the two copper ions in the dimer smears out the lines caused by the hyperfine splittings. Upon the addition of one drop of pyridine, however, the ESR spectrum characteristic of the monomeric copper ion was observed. Therefore, it is adequate to mention that the addition of pyridine to the toluene solution of **9** has led to the dissociation of the dimer to the monomer, probably ligated by the pyridine molecule, as is shown in Scheme 1. Previously it has been shown that the temperature dependence of the magnetic susceptibility of **9** could be well-interpreted by the dimeric model with ferromagnetic exchange interaction of the order of 20 K. Therefore, it is plausible to consider that **9** retains the dimeric structure even in the toluene solution. On the other hand, the ESR spectrum of the triplet state observed in **10**, indicates that **10** makes a dimer in the microcrystalline state. However, the ESR spectrum of **10** in the toluene solution showed the hyperfine structure characteristic of the monomeric copper ion at room temperature and at that of liquidnitrogen. The half-field resonance giving one evidence of the dimeric interaction was not observed in the toluene solution, even at the temperature of liquidnitrogen. These results suggest that the dimer of the **10** formed in the microcrystalline state dissociates into two monomeric species in the toluene solution, as is shown in Scheme 1. Such a difference between **9** and **10** in the toluene solutions may be due to the difference in ligation ability between -COOH and -OH. Consequently, the complexes belonging to Group III can be characterized as those in which the complexes have the dimeric structure in the solid state.



Scheme 1.

Unfortunately, we could not obtain the useful information from the ESR spectra of **9** and **10**, about the circumstances of the copper ions in the dimer. However, the fact that the ESR parameters of the dissociated species of **9** and **10** are very similar to those of the complexes in Group II indicates that the ligand configurations of the copper ions in the dimers are not so different as those of the copper ions belonging to Group II. The substituents of formazan, -COOH and -OH, can be regarded as bases, $-COO^-$ and $-O^-$. On the other hand, the substituent groups in Group I and II can not be bases, though they are electronegative. Therefore. only the ortho substituents, which can be bases for the copper ion, have the possibility of forming magnetically interacted dimeric species.

It is interesting to compare the α^2 and $A_{/\!/}$(Cu) of the present complexes with those of copper-containing proteins. Copper-containing proteins have been classified into three types from the spectroscopic point of view:[20]

Type I: Blue copper proteins. $A_{/\!/}$(Cu) is less than

0.008 cm^{-1}, and there is an abnormally strong absorption maximum around 600 nm.

Type II: Normal copper proteins. The copper splitting constants are of the order of 0.017 cm^{-1}, and the other spectroscopic parameters are similar to those of the copper complexes with a planar structure.

Type III: ESR nondetectable copper proteins. It is generally said that a strong antiferromagnetic or ferromagnetic coupling between two copper ions leads to the ESR spectra becoming nondetectable.

X-Ray analyses were carried out in several kinds of **Type I** copper proteins; the sulfur coordination was thus authenticated.[30,31] Their bonding conditions have become clear.[32] Though sulfurs do not exist in the ligands of the present complexes, the ESR parameters and α^2 values of Group I correspond well to those of **Type I** copper proteins. Therefore, the nitrogens of formazan would constitute strong covalent bondings with the copper ion in the complexes of Group I, as in the case of **Type I** copper proteins. The α^2 values of the ordinary copper complexes with peptide bondings, in which the copper ions have the square-planar symmetry, are in the range from 0.81 to 0.82. The α^2 and $A_{/\!/}$(Cu) values of the complexes of Group II are 0.7 and 0.017 cm^{-1} respectively. Therefore, the complexes of Group II correspond well to the **Type II** copper proteins. It had been considered that the two copper ions were so strongly coupled in the **Type III** copper proteins that ESR observation was difficult. However, the observation of the ESR of the triplet state was accomplished first in the Met derivative of hemocyanine copper, showing clear evidence of the interaction of the two copper ions. As has previously been mentioned in the Results section, the exchange-narrowing was observed in **9** and the ESR spectrum of the triplet state was observed in **10**, in each microcrystalline state. They are characterized as the species with the dimeric interaction, corresponding to **Type III**.

The most characteristic point of these results is that the three types of ESR behaviour, depending upon the different substituent groups to the ortho position of 1-phenyl ring, correspond to the three types of copper proteins. These results may be useful in elucidating the micro-structural details around the copper ions in **Types I, II**, and **III** copper proteins. The 5-formazanyl copper(II) complexes with a flexible molecular structure have the possibility of being plausible model compounds of copper-containing proteins.

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