ESR Studies on Salicylaldehyde Schiff Base Complexes of Copper(II). II.[1] Bis(*N*-cyclohexyl- and *N*-cycloheptyl-salicylideneaminato)copper(II) Complexes and Their Derivatives in Solutions

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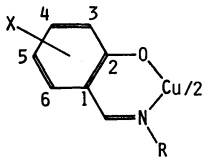
Ten of the title complexes in frozen toluene solutions and occasionally in other solutions have been studied by the ESR method. Most of the complexes showed both monomer and dimer ESR spectra simultaneously, and the equilibrium constant for 2 monomer ⇆ dimer has been determined by analyzing the concentration dependence of the intensity ratios of dimer and monomer ESR signals. The results indicate that the equilibrium constants of the complexes are dependent in a marked but subtle way, not upon the bulkiness of *N*-substituents, but upon both kind and position of the substituents introduced into the ligand benzene rings, and that the equilibrium constants are solvent-dependent. All the observed dimer ESR spectra were similar to each other, and computer simulation analysis of the spectra has revealed that the dimers formed in toluene have the same structures as that in green crystals of bis(*N*-cyclohexylsalicylideneaminato)copper(II). On the other hand, monomers of the title complexes have been found to show various degrees of tetrahedral distortion in the coordination geometry.

The title complexes (I) (abbreviated as Cu(X-sal-R)$_2$†) have various conformations, depending upon R



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and X, and show color isomerism.[2–4] X-Ray structural analyses and ESR studies have confirmed that these complexes are monomeric or dimeric in crystals.[1,5,6] Coordination chemistry of these complexes in solutions is now of great interest. We report here ESR results of these complexes in solutions, especially in toluene, with the intention of elucidating their structures and properties.

Experimental

The same sample complexes as in the previous work were used here.[1] X-Band ESR spectra were measured for the complexes in solutions at the temperature of liquid nitrogen and at room temperature, with a Varian E-4 ESR spectrometer. Commercial Nakarai's "spectrograde" solvents were used without further purification. The solubilities of the complexes in toluene at room temperature were determined spectrophotometrically.

Results and Discussion

Monomeric Complexes. Most of the present complexes in frozen toluene solutions simultaneously showed both monomer and dimer ESR spectra superimposed on each other. In these solutions, monomers and dimers are in equilibrium, since the intensity ratio of dimer and monomer ESR signals for any of the complexes increases with its concentration,[7–9] as exemplified by Fig. 1. On the other hand, Cu(H-sal-Cp)$_2$ and Cu(3-MeO-sal-Ch)$_2$ at any concentration did not show dimer ESR spectra at all, but monomer spectra alone, as shown in Fig. 2; Cu(H-sal-*t*-Bu)$_2$ is just the same in this respect.[10,11] Figure 2(C) is the monomer ESR spectrum of Cu(H-sal-Ch)$_2$. Its line shape was invariant at any low concentration, but is slightly different from those of the other two spectra

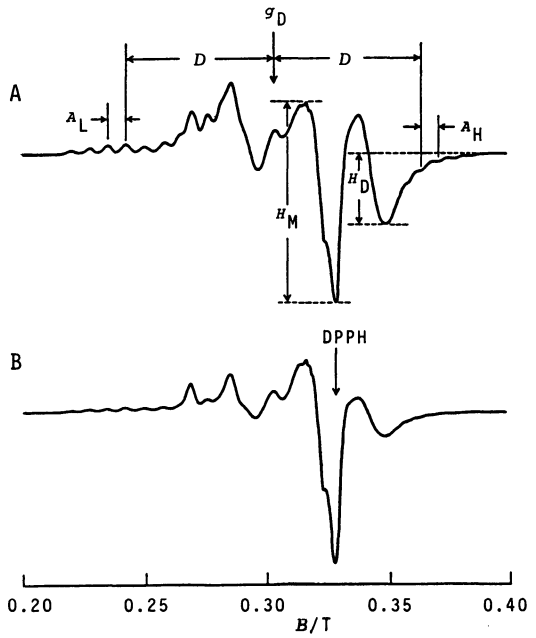

Fig. 1. X-Band ESR spectra of Cu(5-Br-sal-Cp)$_2$ in toluene at 77 K: A, 2.5×10^{-3} M; B, 5.0×10^{-4} M. The parameters of g_D, D, A_L, A_H, H_D, and H_M are defined in A (see text as to the meanings of these parameters).

†The abbreviations of substituents used in this work are as follows: Ch, cyclohexyl; Me$_3$Ch, 3,3,5-trimethylcyclohexyl; Cp, cycloheptyl; Me, methyl; MeO, methoxyl; *i*-Pr, isopropyl; *t*-Bu, *t*-butyl.

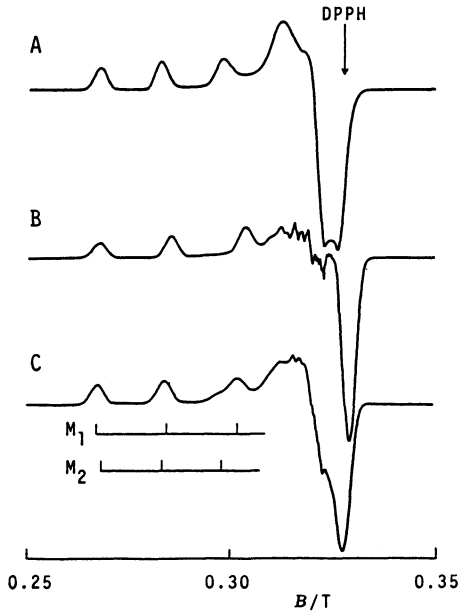

Fig. 2. X-Band ESR spectra of the monomeric Cu(X-sal-R)$_2$ complexes in toluene at 77 K: A, Cu(H-sal-Cp)$_2$, 2.5×10^{-3} M; B, Cu(3-MeO-sal-Ch)$_2$, 2.5×10^{-3} M; C, Cu(H-sal-Ch)$_2$, 5.0×10^{-4} M. In C, the low field spectral part is analyzed as due to two different monomeric species, M_1 and M_2.

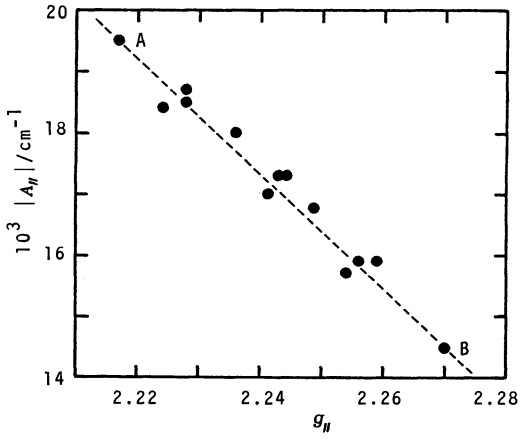

Fig. 3. Plot of $A_{\parallel}$ against $g_{\parallel}$ for the monomeric Cu(X-sal-R)$_2$ complexes; A and B, plots for Cu(H-sal-Me)$_2$ and Cu(H-sal-*t*-Bu)$_2$, respectively; the other plots, from Table 1.

in Fig. 2 at the low field part. These observations are quite similar to those of Cu(H-sal-*i*-Pr)$_2$,[11] showing that there are two different monomeric species for Cu(H-sal-Ch)$_2$ in toluene.

Table 1 summarizes the $g_{\parallel}$ and $A_{\parallel}$ values determined for all the monomeric complexes in frozen toluene solutions, together with the g_0 and A_0 values in fluid toluene solutions at room temperature. A series of Cu(H-sal-R)$_2$ are known to show various degrees of tetrahedral distortion in the coordination geometry, depending upon the bulkiness of R;[11,12] for instance, the dihedral angles between two chelate rings for Cu(H-sal-Me)$_2$ and Cu(H-sal-*t*-Bu)$_2$ in crystals are 0 and 62°, respectively, and the latter is the largest of the structures reported so far.[13] A linear relationship between $g_{\parallel}$ and $A_{\parallel}$ has been demonstrated for these complexes, as shown in Fig. 3 by a dotted straight line drawn through the data of Cu(H-sal-Me)$_2$ and Cu(H-sal-*t*-Bu)$_2$.[12] Plots of the $g_{\parallel}$ and $A_{\parallel}$ values from Table 1 have also been found to fall on the same straight line (Fig. 3), indicating that the present monomeric complexes in toluene show various degrees of the tetrahedral distortion ranging from almost null to that of Cu(H-sal-*t*-Bu)$_2$, in spite of the fact that Ch, Cp, and their derivatives are almost the same in bulkiness.

Dimer Formation Constants. Undoubtedly, a monomer (M)-dimer (D) equilibirum, $2M \rightleftharpoons D$, is established in the solution systems for which both monomer and dimer ESR spectra are simultaneously observed, as has been confirmed so far.[7-9] The value of $R=H_D/H_M \propto [D]/[M]$ can be directly obtained from each spectrum, where H_D and H_M are the peak heights of any specific dimer and monomer ESR signals,

Table 1. Monomer ESR parameters[a]

Cu(X-sal-R)$_2$ X	R	$g_{\parallel}$	$10^4\,\lvert A_{\parallel}\rvert$ / cm^{-1}	g_0	$10^4\,\lvert A_0\rvert$ / cm^{-1}
H	Ch[b]	2.236	180	2.119	66
		2.254	157		
5-Cl	Ch	2.241	170	2.119	67
5-Br	Ch	2.243	173	2.119	64
5-NO_2	Ch	2.252	167	2.120	67
H	Me_3Ch	2.228	185	2.117	67
3-MeO	Me_3Ch	2.224	184	2.115	68
5,6-benzo	Ch	2.228	187	2.114	68
H	Cp	2.256	159	2.119	66
5-Cl	Cp	2.259	159	2.116	62
5-Br	Cp	2.244	173	2.119	65

a) The $g_{\parallel}$ and $A_{\parallel}$ values were determined from frozen toluene solution ESR spectra at 77 K, and the g_0 and A_0 values, from fluid toluene solution ESR spectra at room temperature. b) Two different species were identified.

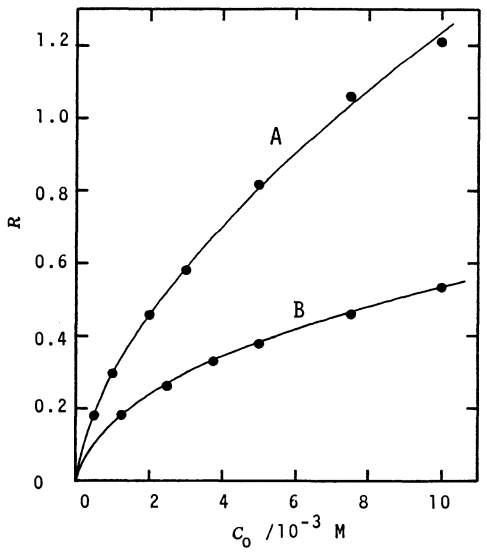

Fig. 4. Relationship between R and C_0 for Cu(5-Br-sal-Ch)$_2$ (A) and Cu(5-Cl-sal-Ch)$_2$ (B): (●), experimental; (——), calculated (see text).

respectively. Then, R is expressed as

$$R = (\sqrt{8KC_0+1}-1)/P$$

where K is the equilibrium or dimer formation constant, P the proportionality constant and C_0 the total concentration. K and P can be determined by fitting the above equation to experimental plots of R against C_0. The observation was made by quickly freezing a toluene solution in liquid nitrogen, using quartz sample tubes of the same size. The equilibrium constant obtained, therefore, is considered to be pertinent for a temperature somewhat lower than the freezing point of toluene. Throughout this work, the monomer and dimer ESR signals used for the determination of H_M and H_D respectively were selected as shown in Fig. 1. All the K, P, R, and C_0 values, together with the solubilities of the complexes in toluene, are listed in Table 2. Two examples of experimental plots of R against C_0 and their fitting curves are given in Fig. 4 for illustration.

As to the dimerization ability of the present complexes, much is elucidated from Table 2. Cu(H-sal-Cp)$_2$ has no dimerization ability, but its 5-halogeno derivatives have. Similarly, the 5-halogeno derivatives of Cu(H-sal-Ch)$_2$ dimerize much more easily than the parent complex. Cu(H-sal-Me$_3$Ch)$_2$ can dimerize a little more easily than Cu(H-sal-Ch)$_2$, but these complexes are roughly comparable in the K value to Cu(H-sal-Me)$_2$.[9] These facts indicate that the apparent bulkiness of N-substituents is not an important factor in the dimerization, except for N-t-Bu; not only Cu(H-sal-t-Bu)$_2$ but also its 5-halogeno and 5-NO$_2$ derivatives were found to have no dimerization ability. The intrinsic nature of the present dimerization, however, is so subtle that, for the 5-Cl and 5-Br derivatives of Cu(H-sal-Ch)$_2$, the former has a much larger K value than the latter, while, for those of Cu(H-sal-Cp)$_2$, the reverse is observed. It is noteworthy that drastic changes of K from 75 to 8.5×10^3 and 1.4×10^5 M^{-1} are brought about only by the introduction of 5-Cl and 5-NO$_2$ respectively into Cu(H-sal-Ch)$_2$. Similar enhancing effects of the nitro group on the dimerization ability of other kinds of planar complexes have been reported so far.[9,10] The K values of Cu(H-sal-Me)$_2$ and of its 5-Me, 5-Br, and 5-MeO derivatives were determined to be 2.4×10^2, 1.8×10^2, 2.3×10^3, and 2.1×10^3 M^{-1}, respectively;[8] clearly, the latter two are larger than the former two. The NO$_2$ and MeO substituents are representative π-electron-withdrawing and donating groups, respectively, and the halogeno substituents are also typical functional groups with remarkable substituent effects. From these facts it is clear that such influential groups as halogens, NO$_2$, and MeO at the 5-position have a common substituent effect of enhancing the present dimerization ability

Table 2. Values[a] of K, P, and R and solubility[b]

Cu(X-sal-R)$_2$		K	P	$R(10^3C_0)$[c]	Solubility
X	R	M^{-1}		M	M
H	Ch	75	38	0.068(20.00); 0.057(15.00); 0.043(10.00); 0.026(5.00); 0.016(2.50)	0.039
5-Cl	Ch	8,500	47.0	0.535(10.00); 0.460(7.50); 0.380(5.00); 0.331(3.75); 0.260(2.50); 0.180(1.25)	0.042
5-Br	Ch	800	5.82	1.210(10.00); 1.050(7.50); 0.814(5.00); 0.585(3.00); 0.458(2.00); 0.296(1.00); 0.180(0.50)	0.018
5-NO$_2$	Ch	140,000	1,200	0.017(0.40); 0.015(0.30); 0.012(0.20)	0.00048
H	Me$_3$Ch	105	67	0.100(68.8); 0.083(51.6); 0.065(34.4); 0.045(17.2); 0.027(8.6)	0.20
3-MeO	Me$_3$Ch	0			>0.75
5,6-benzo	Ch	140	34	0.032(2.98); 0.024(1.99); 0.013(1.00)	0.0047
H	Cp	0			0.13
5-Cl	Cp	44	55	0.052(40.0); 0.044(30.0); 0.034(20.0); 0.020(10.0)	0.094
5-Br	Cp	2,400	16.6	0.541(5.12); 0.490(4.26); 0.434(3.41); 0.373(2.56); 0.291(1.71); 0.191(0.85); 0.125(0.43)	0.029

a) See text as to the definition of K, P, and R. b) Solubility in toluene at room temperature. c) $R(C_0)$ expresses the observed R value at the total concentration of C_0.

Table 3. Dimer ESR parameters[a)]

Cu(X-sal-R)$_2$ X	R	Medium[b)]	g_D	10^3D	10^3A_L	10^3A_H
				cm^{-1}		
H	Ch	Toluene	2.172	62.4	7.6	6.6
		Polycrystal	2.11	61		
5-Cl	Ch	Toluene	2.172	61.4	7.8	7.0
		Polycrystal	2.16	62	7.6	
5-Br	Ch	Toluene	2.168	61.3	7.6	6.6
5-NO_2	Ch	Toluene	2.201	58.1	8.0	5
H	Me_3Ch	Toluene	2.172	59.1	7.8	6.6
5,6-benzo	Ch	Toluene	2.169	58.6	8.6	6.7
5-Cl	Cp	Toluene	2.168	61.2	7.6	6.6
5-Br	Cp	Toluene	2.172	61.7	7.6	6.8
		Polycrystal	2.15	62	8	
Calcd[c)]			2.169	62.0	8.0	6.6

a) See text (Fig. 1) as to the definition of dimer ESR parameters. b) Medium at 77 K. c) Values derived from the computer simulation spectrum (Fig. 5(A)), which was calculated with the following parameters, assuming a parallel planar dimer: $g_{\parallel}$=2.245, $g_{\perp}$=2.050, $A_{\parallel}$=0.0087 cm^{-1}, $A_{\perp}$=0.0015 cm^{-1}, r=3.67 Å, ξ=37°, ΔH_1=2.5 mT, ΔH_2=2.2 mT (ΔH_1, ΔM=1 spectral line width).

markedly. On the other hand, Cu(3-MeO-sal-Me_3Ch)$_2$ has no dimerization ability, as well as Cu(3-MeO-sal-Me)$_2$;[8)] furthermore, the K value of Cu(3-Me-sal-Me)$_2$ is smaller than that of Cu(H-sal-Me)$_2$,[8)] suggesting the possibility that 3-substituents depress the dimerization. Cu(5,6-benzo-sal-Ch)$_2$ dimerizes about twice more easily than Cu(H-sal-Ch)$_2$, suggesting that the enlargement of ligand π-electron systems may be a favorable factor in this dimerization, in conformity with the general belief that stacking interaction between planar molecules with π-electron systems is stronger, as the π-electron sytems are larger. In conclusion, there are remarkable substituent effects on the present dimerization ability, but further work is needed to analyze the dimerization ability in more detail.

Interestingly, Table 2 indicates that there is a tendency for the K value to increase with a decrease in the solubility. This seems to be qualitatively understandable from the generality that the solubility is lower, as the intermolecular interaction is stronger.

Dimeric Structures. The present dimer ESR spectral features can be described by the dimer ESR parameters, g_D, D, A_L, and A_H, which are defined in Fig. 1. Table 3 summarizes all these parameter values determined from frozen toluene solution spectra, together with those from several powder spectra.[1)] Inspection of this table indicates that all the dimers are essentially similar in structure, becasue their dimer ESR parameters are almost similar to each other. These dimer ESR spectra can be analyzed by the computer simulation method, assuming a parallel planar dimer with the distance (r) of 3.67 Å between the two copper atoms and the angle (ξ) of 37° between the $g_{\parallel}$ axis and the copper–copper axis, as has been applied previously;[14,15)] the simulation spectrum thus obtained is shown in Fig. 5(A), which approximately reproduces the observed spectrum of Cu(5-Br-sal-Ch)$_2$ (Fig. 5(B)). The dimer ESR parameters determined from this simulation spectrum are in good agreement with the observed ones, as shown in Table 3.

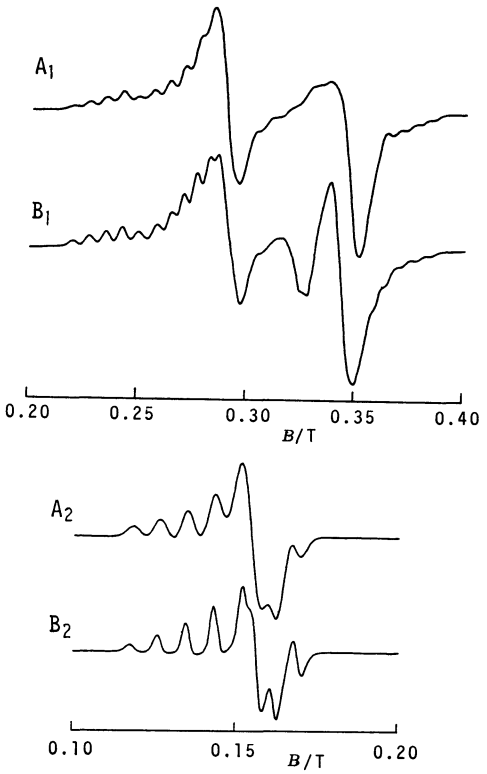

Fig. 5. Comparison between simulated and experimental dimer ESR spectra; A_1 and A_2, simulation spectra, calculated with the parameters of $g_{\parallel}$=2.245, $g_{\perp}$=2.050, $A_{\parallel}$=0.0087 cm^{-1}, $A_{\perp}$=0.0015 cm^{-1}, r=3.67 Å, ξ=37°, ΔH_1=2.5 mT, ΔH_2=2.2 mT, ν=9.23 GHz (the suffixes 1 and 2 correspond to ΔM=1 and 2 spectra, respectively; ΔH, line width; see text as to details of the computer simulation); B_1 and B_2, observed spectra for Cu(5-Br-sal-Ch)$_2$ in almost saturated toluene solutions at 77 K.

Interestingly, an X-ray crystal structure determina-

tion of green Cu(H-sal-Ch)$_2$ has revealed that the molecules exist as dimers of an approximately parallel planar type with r=3.38 Å and ξ=36°; actually, the monomeric halves of the dimers do not have a planar coordination geometry, but a somewhat tetrahedrally-distorted one with a dihedral angle of about 30°.[6] These r and ξ values are in fair agreement with those estimated above by the computer simulation method, in consideration of a point-dipole approximation used in the simulation in which the r value is generally estimated to be several % larger than the actual one.[16] Now, it is reasonably concluded that all the dimers formed in toluene have the same structures as that in green Cu(H-sal-Ch)$_2$ crystals.††

Solvent Effects of Dimerization. The dimer formation constants of the present complexes are remarkably solvent-dependent, as is usual with many other analogous systems.[15,18] The R values of Cu(5-Br-sal-Ch)$_2$ at 0.0050 M (1 M=1 mol dm^{-3}) in the mixtures of 4 parts of toluene and 1 part of pyridine, *N*,*N*-dimethylformamide (DMF), dichloromethane, methanol, and dimethyl sulfoxide (DMSO) were changed into 0, 6, 20, 38, and 98% of that in pure toluene, respectively. Interestingly, DMSO has almost no effects on the dimer formation, while DMF remarkably depresses it, in spite of both solvents being nearly equal in the basicity or donicity.[19] It seems likely that the above difference between DMSO and DMF is attributed to the presence of a π-system in the DMF molecule, because the so-called π-π interaction is considered as an important driving force for the dimerization of complexes with π-ligands; depressing effects of DMF on this kind of dimerization will be discussed elsewhere in more detail. Pyridine completely inhibits the dimerization by its strongly coordinating ability, the resultant complexes probably being sterically difficult of dimerization. It is to be noted that dichloromethane and methanol also have depressing effects on the dimerization. The solubility of Cu(5-Br-sal-Ch)$_2$ in methylcyclohexane, the saturated hydrocarbon of toluene, is remarkably low, compared with that in toluene. Accordingly, the dimer formation constant in methylcyclohexane was apparently larger than that in toluene, in agreement with the expectation discussed above.

†† As seen in Table 3, green Cu(H-sal-Ch)$_2$ in polycrystals is somewhat different in the g_D value from others, but this might be a result of intricate magnetic interaction among dimers in the crystals.[1,17]

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