ESR Studies on Salicylaldehyde Schiff Base Complexes of Copper(II). III.[1] Dimer Formation on Bis(*N*-alkylsalicylideneaminato)-copper(II) Complexes and Their Derivatives in Toluene

Hiroshi Yokoi,* Akira Takeuchi,† and Shoichiro Yamada†
Department of Applied Chemistry, Faculty of Engineering, Shizuoka University, Hamamatsu 432
†Institute of Chemistry, College of General Education, Osaka University, Toyonaka 560

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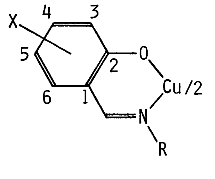
Twenty one of the title complexes (abbreviated as Cu(X–sal–R)$_2$; X=H, 5-Cl, or 5-Br and R=*N*-alkyl) in toluene have been extensively studied by the ESR method in order to obtain fundamental information on dimer formability and the dimeric structures of these complexes. The equilibrium constant (*K*) for 2 monomer $\rightleftharpoons$ dimer has been determined by analyzing the concentration dependence of the intensity ratios of the dimer to the monomer ESR signals for frozen toluene solutions. The *K* values of the Cu(H–sal–R)$_2$ complexes are remarkably R-dependent as follows: methyl (233)≫ethyl (10)~isobutyl (9)>other normal alkyl groups (~4) for a series of the R groups with primary α-carbons, and cyclohexyl (75)≫isopropyl (7)>*s*-butyl (≪1)>cycloheptyl (~0)> *t*-butyl (0) for a series of the R groups with secondary and tertiary α-carbons, where the complex is denoted by R, followed by *K* (M^{-1}) in parentheses. The complexes with R=nonyl or higher homologues form some polymeric species besides dimers and monomers. The *K* values remarkably increase by the introduction of X=5-Cl or 5-Br. The observed dimer ESR spectra have been analyzed by computer simulation in order to estimate the structural parameters (r and ξ) of parallel-planar dimers, where r is the Cu–Cu distance and ξ is the angle between the Cu–Cu direction and the normal to the molecular plane. These results indicate that most complexes form two types of dimers with different structures: type a, r=3.75 Å and ξ=37°; type b, r=4.10 Å and ξ=23°. The Cu(X–sal–methyl)$_2$ complexes form only a-type dimers, while the others simultaneously form both types of dimers, except the complexes of R=isopropyl and cyclohexyl which form another type of parallel-planar dimers having a slightly tetrahedrally-distorted coordination geometry around each copper atom.

Many copper(II) complexes with bidentate *N*-substituted salicylideneamines and their derivatives (abbreviated as Cu(X–sal–R)$_2$, I) are dimeric in crystals and have the ability to form dimers in solutions.[1–8] These dimers are of a so-called parallel-planar type. In this work, the R- and X-dependences of dimer formability and dimeric structures for the Cu(X–sal–R)$_2$ complexes of R=alkyl group and X=H, 5-Cl or 5-Br in toluene have been extensively investigated by the ESR method.



I

Experimental

All of the sample complexes (17 complexes listed in Table 1 and four complexes of R=nonyl, decyl, dodecyl, and hexadecyl) were prepared and purified according to the methods described in the literature,[9] using commercially available reagents. Commercial Nakarai's "spectrograde" toluene was used as a solvent without further puification. The X-band ESR spectra for frozen toluene solutions at 77 K were measured with a JEOL Model JES-FE2XG ESR spectrometer; a Takeda Riken TR-5501 frequency counter and an ECHO Electronics EFM-2000 NMR field meter were used in measurements of the microwave frequency and magnetic fields, respectively. A computer simulation of the dimer ESR spectra was carried out at the Computer Center of Tohoku University, using a program based on the point-dipole approximation.[6]

Results and Discussion

Dimer Formation Constants. Most of the present complexes in frozen toluene solutions simultaneously show both monomer and dimer ESR spectra superimposed on each other, as exemplified in Fig. 1. This fact indicates that a monomer(M)–dimer(D) equilib-

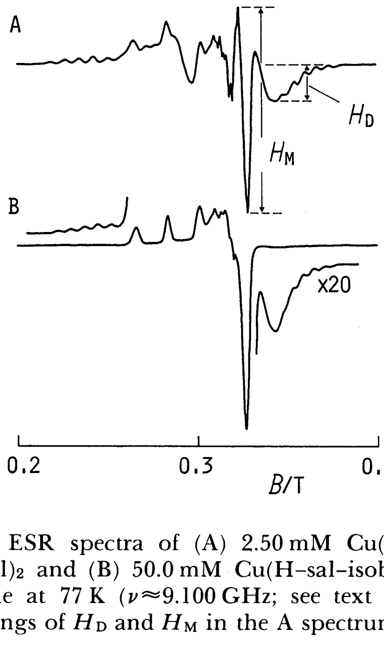


Fig. 1. ESR spectra of (A) 2.50 mM Cu(5-Cl-sal-methyl)$_2$ and (B) 50.0 mM Cu(H-sal-isobutyl)$_2$ in toluene at 77 K (ν≈9.100 GHz; see text as to the meanings of H_D and H_M in the A spectrum).

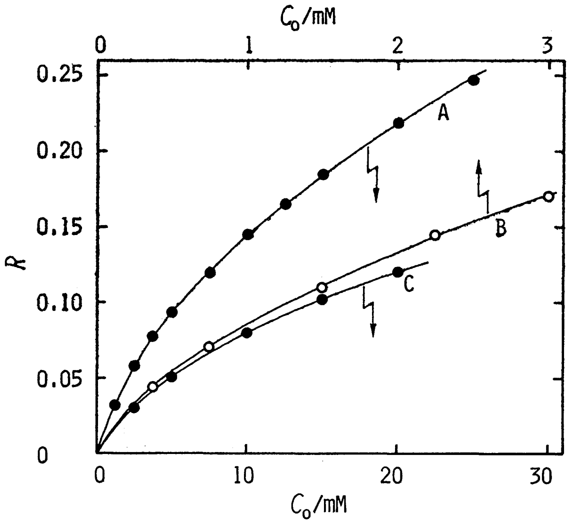


Fig. 2. Relationship between R and C_0 for the Cu(X-sal-R)$_2$ complexes ((○), experimental; (——), calculated (see text)): A, X=H, R=methyl; B, X=5-Br, R=methyl; C, X=5-Br, R=hexyl.

Table 1. Values of K and P[a]

Cu(X-sal-R)$_2$ X	R	K M^{-1}	P
H	Methyl	233	23.8
5-Cl	Methyl	830	20.1
5-Br	Methyl	992	23.3
H	Ethyl	10	59
H	Propyl	3.8	40
H	Isopropyl	7.0	238
H	Butyl	2.4	30
H	Isobutyl	8.9	72
H	s-Butyl	≪1	
H	t-Butyl	0	
H	Pentyl	4.0	42
H	Hexyl	3.4	50
5-Cl	Hexyl	140	37.2
5-Br	Hexyl	177	36.8
H	Cyclohexyl	75	38[b]
H	Cycloheptyl	0[b]	
H	Octyl	4.0	87[c]

a) Errors: ±10% and ±25% for the values of three and two significant figures respectively. b) From Ref. 1. c) The $I=-3/2$ hyperfine line of $A_{\parallel}$ in the monomer spectrum was selected for the determination of H_M.

rium, $2\,M \rightleftharpoons D$, is established in these solutions.[1] The equilibrium or dimer formation constant (K) for a complex can be determined by measuring the ESR spectra in frozen toluene solutions at several different total concentrations (C_0). In each spectrum, the value of $R=H_D/H_M \propto [D]/[M]$ can be directly obtained, where H_D and H_M are the peak heights of any specific dimer and monomer ESR signals, respectively. Then, R is expressed as

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

where P is a proportionality constant.[1] K and P can be determined by fitting the above equation to the experimental plots of R against C_0. The K values, thus obtained, are considered to be pertinent for temperatures near the freezing point of toluene. In most cases, the same dimer and monomer ESR signals as in the proceding work were selected for the determination of H_D and H_M, respectively, as shown in Fig. 1.[1] Several representatives of the experimental plots and their fitting curves are shown in Fig. 2; all of the K and P values, thus determined, are summarized in Table 1, together with some previous data.

An inspection of Table 1 indicates many aspects of dimer formability for the present kind of complexes in toluene. The following orders are obtained regarding the R-dependence of K for the Cu(H-sal-R)$_2$ complexes: methyl (233)≫ethyl (10)≈isobutyl (9)>other normal alkyl groups (≈4) for a series of groups with primary α-carbons, and cyclohexyl (75)≫isobutyl (7)>s-butyl (≪1)>cycloheptyl (≈0)≥t-butyl (0) for a series of groups with secondary or tertiary α-carbons, where the complex is denoted by R, followed by K in parentheses. These results indicate that the K value remarkably varies according to how many β-carbons there are in the R group, as shown by the drastic changes in K with the R-substitutions of methyl for ethyl and of isopropyl for t-butyl. The remarkable difference between isopropyl (7) and t-butyl (0) suggests that the isopropyl group in the dimer may be held in a fixed configuration without free rotation, since the freely rotating isopropyl group must be almost equivalent in sterical effects to the t-butyl group. The cyclohexyl group can not freely rotate in its complex, but is held in such a fixed configuration as that found for the dimer in crystals.[4] The present result regarding cycloheptyl (≈0) also seems to be consistent with the general belief that the seven-membered ring of cycloheptyl is more flexible than the six-membered one of cyclohexyl, and is closer to the t-butyl group with regard to steric effects. All of these findings indicate that the K value of Cu(H-sal-R)$_2$ is not always dependent upon the apparent bulkiness of R.

A remarkable dependence of X on K is also shown in Table 1. The introduction of X=5-Cl or 5-Br into Cu(H-sal-R)$_2$ enhances dimer formability almost 4-fold and 45-fold for the cases of R=methyl and hexyl, respectively. A similar sort of enhancement caused by the same substitution was also observed for the cases of R=cyclohexyl and cycloheptyl.[1] On the other hand, Cu(H-sal-t-butyl)$_2$ did not show dimer formation at all, even upon the introduction of 5-Cl or 5-Br, although both Cu(H-sal-R)$_2$ with R=t-butyl and cycloheptyl have no capability to form dimers. This fact suggests that whether the α-carbon of R is of a tertiary or secondary class is definitely important in the present dimer formation. Though the *t*-butyl group, essentially, has a completely inhibitory effect on the dimer formation, probably due to a steric hindrance, the cycloheptyl group does not always do so; this indicates that this group can also adopt a fixed configuration favorable to dimerization, as well as other groups with secondary α-carbons, in case of the presence of a strong attractive interaction between monomeric halves in the dimerization.

Formation of Mulinuclear Species. The ESR spectra observed for the Cu(H–sal–R)$_2$ complexes of R=n-$\mathrm{C}_m\mathrm{H}_{2m+1}$ ($m \geqq 9$) were different in line shape from those shown above, as exemplified by Fig. 3, where no signal peak around the position marked by an arrow was observed. This change in line shape apparently results from the appearance of a single broad spectrum superimposed on both the dimer and the monomer spectra. The relative intensity of this single broad spectrum increases as the normal alkyl group becomes a higher homologue; the spectrum alone comes to appear in almost a complete line shape in case of R=hexadecyl, as shown in Fig. 3. The spectrum of Fig. 3C, line shape of which is typical of an aggregation of the complex molecules, is not the same as that in polycrystals. In this study, however, we interpreted the spectrum of Fig. 3C as being due to some polymers which result from a molecular association going beyond dimerization. The fact that the formation of these polymers occurs only for R=n-$\mathrm{C}_m\mathrm{H}_{2m+1}$ ($m \geqq 9$) suggests that such a molecular association may apparently be induced by an associative interaction among these long normal alkyl chains in toluene.

Dimeric Structures. The dimer ESR spectrum of Cu(H–sal–methyl)$_2$ in frozen toluene solutions has been analyzed in full detail by the computer simulation method,[6] in which the coordinate of dimers is of a parallel-planar type with the structural parameters of r and ξ (r, the Cu–Cu distance; ξ, the angle between the Cu–Cu direction and the normal to the molecular plane) and in which a point-dipole approximation is used. As a result, r=3.75 Å and ξ=37° have been determined for the above dimer. The dimeric structure, thus estimated, is concluded to be similar, but not equal, to that in γ-form crystals (r=3.34 Å and ξ=60°),[3] even though errors due to the point-dipole approximation is taken into account.[10] Some of ΔM=1 and 2 spectra observed here, together with those of Cu(H–sal–methyl)$_2$, are shown in Figs. 4 and 5 respectively, where all of the ΔM=1 spectra (Fig. 4) represent overlapping curves of the dimer and monomer spectra, as has already been described. Figure 5B is apparently similar to Fig. 5A, though a closer inspection of the line shape of the former spectrum indicates the superimposition of another slightly different ΔM=2 spectrum at a low intensity ratio. Figure 5C shows this superimposition more clearly. In conclusion, the spectra for the Cu(X–sal–R)$_2$ complexes with R=ethyl, other normal alkyls, and isobutyl consist of two spectra of types a and b overlapping at various intensity ratios, where the positions of some hyperfine lines due to the spectra of

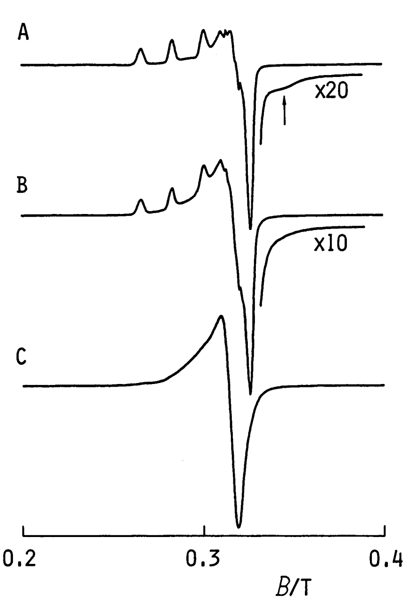


Fig. 3. ESR spectra of the Cu(H–sal–R)$_2$ complexes in toluene at 77 K (C_0=12.5 mM; $\nu \approx$9.100 GHz): A, R=decyl; B, R=dodecyl; C, R=hexadecyl (see text as to the meaning of an arrow shown in the A spectrum).

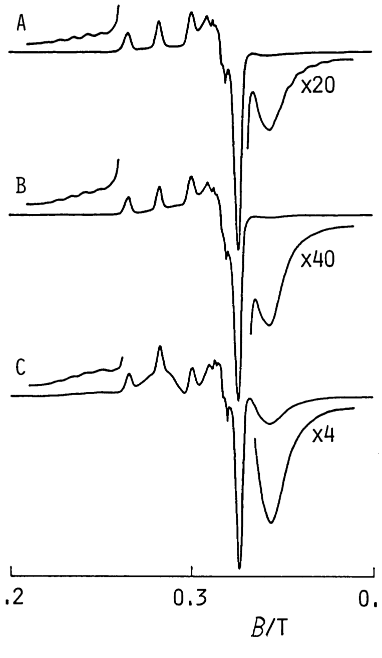


Fig. 4. ESR spectra (ΔM=1) of the Cu(X–sal–R)$_2$ complexes in toluene at 77 K ($\nu \approx$9.100 GHz): A, X=H, R=propyl (50.0 mM); B, X=H, R=hexyl (50.0 mM); C, X=5-Br, R=hexyl (20.0 mM).

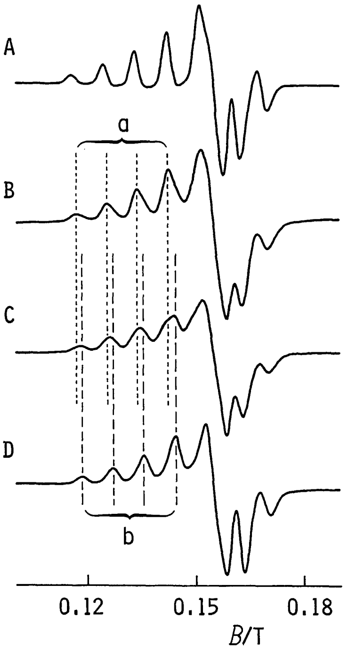


Fig. 5. ESR spectra ($\Delta M=2$) of the Cu(X-sal-R)$_2$ complexes in toluene at 77 K ($\nu \approx 9.100$ GHz); A, X=H, R=methyl; B, X=H, R=propyl; C, X=H, R=hexyl; D, X=5-Br, R=hexyl. See text as to a and b in the figure.

types a and b are expressed by dotted and dashed lines, respectively, in Fig. 5. A comparison of Fig. 5C with Fig. 5D clearly shows that the b-type spectrum is preferentially observed for Cu(5-Cl- or 5-Br-sal-hexyl)$_2$; this is considered to be another effect of 5-Cl and 5-Br. A similar observation is also true of the $\Delta M=1$ dimer ESR spectra. Figure 4C is different in hyperfine structures from Fig. 4A in both ranges 0.22—0.26 T and 0.34—0.38 T. The dimer ESR spectrum of Fig. 4B is eventually regarded as an appropriate superimposition of those of Figs. 4A and 4C, which may be close to the $\Delta M=1$ dimer spectra corresponding to types a and b, respectively.

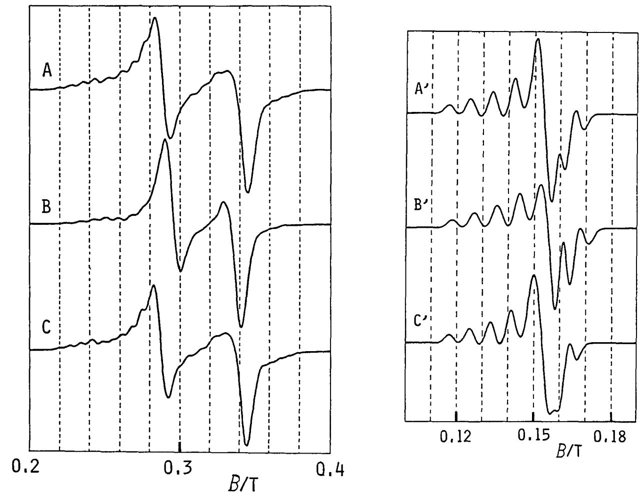


Fig. 6. Dimer ESR spectra simulated with the following parameter values: A and A′, $r=3.75$ Å, $\xi=37°$, $g_{\parallel}=2.235$, $g_{\perp}=2.05$, $A_{\parallel}=0.0087$ cm^{-1}, $A_{\perp}=0.001$ cm^{-1}, $\Delta H_1=2.7$ mT, $\Delta H_2=1.7$ mT; B and B′, $r=4.10$ Å, $\xi=23°$, $g_{\parallel}=2.235$, $g_{\perp}=2.05$, $A_{\parallel}=0.0091$ cm^{-1}, $A_{\perp}=0.001$ cm^{-1}, $\Delta H_1=3.0$ mT, $\Delta H_2=1.9$ mT; C and C′, $r=3.75$ Å, $\xi=37°$, $g_{\parallel}=2.255$, $g_{\perp}=2.055$, $A_{\parallel}=0.0082$ cm^{-1}, $A_{\perp}=0.001$ cm^{-1}, $\Delta H_1=2.5$ mT, $\Delta H_2=1.7$ mT ($\nu=9.100$ GHz; ΔH_1 and ΔH_2 refer to the Gaussian line widths of $\Delta M=1$ and 2 spectra, respectively; all the above A' values are those of triplet-state copper(II) dimers, which are given as one-half of the absolute A values of their monomeric copper(II) complexes).

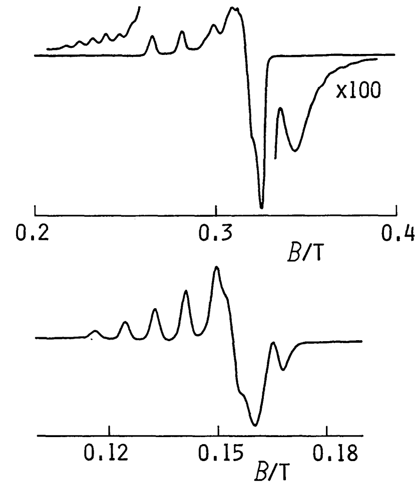


Fig. 7. ESR spectra of Cu(H-sal-isopropyl)$_2$ in toluene at 77 K (50.0 mM; $\nu=9.1035$ GHz).

Simulation spectra for the dimer ESR spectra of types a and b are shown in Figs. 6A and 6B. The r and ξ values estimated here (see the caption of Fig. 6) indicate that the dimeric structure of type a is almost the same as that estimated for Cu(H-sal-methyl)$_2$, and that there is a relation: $r_a < r_b$ and $\xi_a > \xi_b$, where suffixes a and b refer to dimers of types a and b, respectively. This relation is consistent with the general trend of dimeric structures so far recognized.[8] It is of interest that most of the present complexes in toluene form two slightly different dimers of types a and b, both of which must not largely differ in the dimerization energy. A similar phenomenon has also been found for the dimerization of some copper(II) complexes of β-diketones.[11] Furthermore, we have found that the Cu(X-sal-methyl)$_2$ complexes with X=H, 5-Cl, and 5-Br show the same dimer spectra, in spite of these halogen substituents having a remarkably enhancing effect on the dimer formability. This suggests that the dimers of these three complexes are the same in the interaction mode between monomeric halves, but may be different in degree. On the other hand, Cu(H-sal-isopropyl)$_2$ has another dimeric structure, as evidenced by its ESR spectra and the simulation spectra in Figs.

7, 6C, and 6C′. From the r and ξ values estimated here, together with the $g_{\parallel}$ (2.255) and $|A_{\parallel}|$ (160×10^{-4} cm^{-1}) values which are a little larger and smaller respectively than the others',[1] it is concluded that this complex forms another type of parallel-planar dimer in which each copper atom has a slightly tetrahedrally-distorted coordination geometry. This type of dimeric structure has actually been found for Cu(H-sal-cyclohexyl)$_2$ in crystals.[4] Interestingly, the dimer ESR spectra observed for the Cu(H-sal-R)$_2$ complexes with R= cyclohexyl and isopropyl were almost the same in toluene: the latter spectrum was approximately simulated with parameters of r=3.75 Å and ξ=37°.

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