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

Akira Takeuchi, Shoichiro Yamada, and Hiroshi Yokoi[†],*
Institute of Chemistry, College of General Education, Osaka University, Toyonaka, Osaka 560
[†]*Chemical Research Institute of Non-aqueous Solutions, Tohoku University, Sendai 980*
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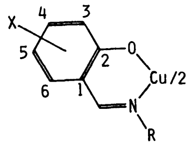
Twelve of the title complexes including color isomers show powder ESR spectra of various line shapes. These complexes are a novel series of copper(II) complexes which have very weak intermolecular spin-exchange interactions in crystals. Brown complexes and most green complexes show monomer and dimer ESR spectra, respectively. It is demonstrated by ESR measurements that the above green complexes are transformed into the brown ones only by grinding those green crystals finely and forcefully with agate mortar and pestle.

There have been many works showing that metal(II) complexes with bidentate *N*-substituted salicylideneamines (I) (abbreviated as M(X-sal-R)$_2$) have various configurations, depending upon R and X.[1-3] These



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complexes often show color isomerism. This kind of studies about the copper(II) complexes can also be carried out by the ESR method in new and interesting aspects. The purpose of this paper is to report powder ESR results for twelve of the complexes, in connection with their structures and properties in crystals. In this work, the complexes with R=cyclohexyl, 3,3,5-trimethylcyclohexyl, and cycloheptyl (abbreviated as Ch, Me$_3$Ch, and Cp, respectively) have been dealt with.

Experimental

All the salicylaldehyde Schiff base complexes of copper(II) were prepared according to the literature,[4] using commercially available reagents. Color isomers for some of the complexes were obtained as previously reported.[5] Twelve complexes prepared in this work are as follows: green Cu(H-sal-Ch)$_2$, brown Cu(H-sal-Ch)$_2$, green Cu(5-Cl-sal-Ch)$_2$, brown Cu(5-Cl-sal-Ch)$_2$, brown Cu(5-Br-sal-Ch)$_2$, green Cu(5-NO$_2$-sal-Ch)$_2$, greenish brown Cu(H-sal-Me$_3$Ch)$_2$, brown Cu(3-MeO-sal-Me$_3$Ch)$_2$, olive brown Cu(5,6-benzo-sal-Ch)$_2$, brown Cu(H-sal-Cp)$_2$, green Cu(5-Cl-sal-Cp)$_2$, and green Cu(5-Br-sal-Cp)$_2$, where Cu(5,6-benzo-sal-Ch)$_2$ denotes bis(*N*-cyclohexyl-2-hydroxy-1-naphthylmethyleneaminato)-copper(II).

X-Band ESR spectra for the above complexes in polycrystals were measured at room temperature and at the temperature of liquid nitrogen with a Varian E-4 ESR spectrometer. Sample powders for ESR measurements were obtained by grinding crystals of the complexes with agate mortar and pestle.

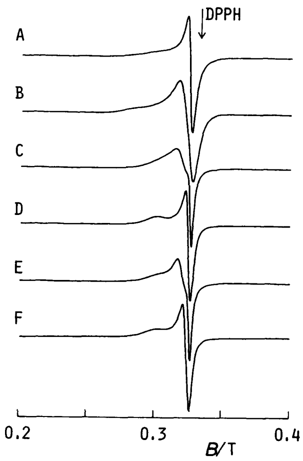

Fig. 1. Powder ESR spectra (X-band; room temperature); A, brown Cu(H-sal-Ch)$_2$; B, brown Cu(H-sal-Me$_3$Ch)$_2$; C, brown Cu(H-sal-Cp)$_2$; D, brown Cu(5-Cl-sal-Ch)$_2$; E, brown Cu(5-Br-sal-Ch)$_2$; F, green Cu(5-NO$_2$-sal-Ch)$_2$.

Results and Discussion

Powder ESR Spectra. The powder ESR spectra of the present complexes at room temperature have a wide variety of line shapes, as shown in Figs. 1—5. These spectra had almost no temperature dependence.

Figure 1 shows the powder ESR spectra of five brown or brownish complexes and green Cu(5-NO$_2$-sal-Ch)$_2$. These spectra appear within a comparatively narrow field range 0.26—0.35 T, and are of a common spectral type for polycrystals of monomeric copper(II) complexes,[6] except that the spectra are very broad in line shape. Brown Cu(H-sal-Ch)$_2$, one of the complexes in Fig. 1, really has one monomeric molecule in the unit cell, as determined by X-ray structural analysis;[7] interestingly, this complex has planar coordination. The spectra in Fig. 1 are so broad in line shape that *g* anisotropies are barely observed. This line broadening is probably due to insufficient spin-exchange narrowing toward the coalescense of four copper hyperfine lines to a single line, meaning that intermolecular spin-exchange interaction energies (*J*)

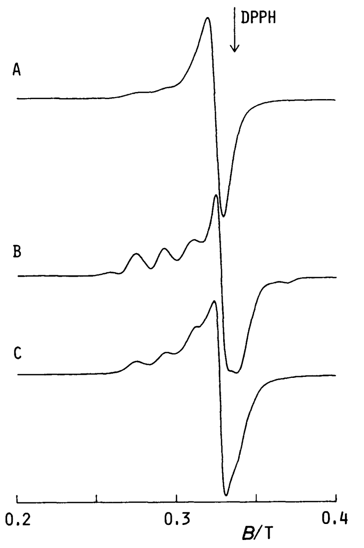

Fig. 2. Powder ESR spectra (X-band; room temperature); A, brown Cu(3-MeO-sal-Me$_3$Ch)$_2$; B, olive brown Cu(5,6-benzo-sal-Ch)$_2$ (softly and coarsely ground powder); C, olive brown Cu(5,6-benzo-sal-Ch)$_2$ (forcefully and finely ground powder).

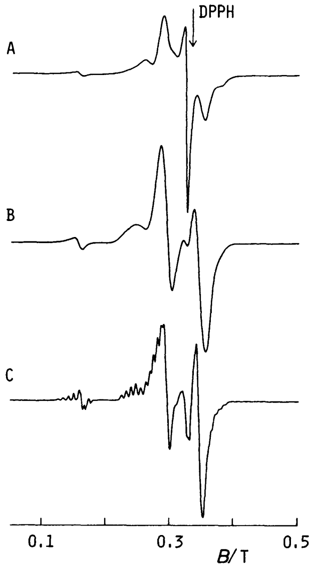

Fig. 3. Powder ESR spectra (X-band; room temperature) and frozen solution ESR spectrum (X-band; 77 K): A, green Cu(H-sal-Ch)$_2$; B, green Cu(5-Br-sal-Cp)$_2$; C, Cu(5-Br-sal-Ch)$_2$ in toluene (almost saturated).

are as small as the order of 0.1 cm^{-1}.[8] On the other hand, in Fig. 2, hyperfine structures are clearly observed in the low-field spectral part. This fact indicates that the complexes of Fig. 2 are monomeric in the crystals with $|J|\lesssim 0.02\,\mathrm{cm}^{-1}$. The existence of such complexes in this series supports the above interpretation of the line broadening in Fig. 1. In Fig. 2(B), extra weak ESR signals at both sides of the monomer signal are clearly observed, but are of obscure origin at present. Further discussion on Fig. 2 (B) and (C) will be given later.

The powder ESR spectra in Fig. 3, whose signals occur over a much wider field range, are quite different in line shape from those in Figs. 1 and 2. The most remarkable feature of Fig. 3(A) and (B) is the appearance of weak half-field signals around 0.15 T. This spectral pattern is typical of triplet-state copper(II) dimers, as evidenced by the fact that Fig. 3(B) is almost identical in line shape with the frozen-solution spectrum of Cu(5-Br-sal-Ch)$_2$ shown in Fig. 3(C), which can be analyzed as a typical dimer spectrum by computer simulation;[9] detailed analyses of this kind of spectra with such well-resolved hyperfine structures as shown in Fig. 3(C) will be given in the next paper in this series of work.[10] Figure 3(B) is of the spectral type accompanying no spin-exchange narrowing effect of hyperfine lines, indicating that the inter-dimer spin-exchange interaction of green Cu(5-Br-sal-Cp)$_2$ is as extremely weak as $|J|\lesssim 0.01$ cm^{-1}. The powder ESR spectra of green Cu(5-Cl-sal-Cp)$_2$ and green Cu(5-Cl-sal-Ch)$_2$ were similar to Fig. 3(A) and (B), respectively. The peak positions of Fig. 3(A) in the range 0.2—0.4 T slightly shifts toward the center, compared with those of Fig. 3(B). This means that the $|J|$ value of the former system is a little larger than that of the latter one. All the copper(II) complexes in this work have thus been found to be a novel series of sample systems which have very weak intermolecular spin-exchange interactions in crystals, suggesting that bulky cyclohexyl and related groups may have some steric effect in breaking easy spin-exchange pathways in crystals. As has been estimated above, green Cu(H-sal-Ch)$_2$ exists as dimers in crystals. This is really consistent with the structural result obtained by X-ray analysis,[11] where monomeric halves in the dimer fundamentally have a flattened tetrahedral coordination. This work has revealed that all the complexes which show dimer ESR spectra are green ones, while brown or brownish complexes show monomer spectra; green Cu(5-NO$_2$-sal-Ch)$_2$ forms an exception, but this might result from some effect of the strong electron-withdrawing group of 5-NO$_2$.

Easy Transformation of Crystal Forms. We have found that some complexes in this study show different powder ESR spectra, according to how finely and forcefully their crystals are ground into powder with agate mortar and pestle, as exemplified in Figs. 2, 4, and 5; this will hereafter be called grinding effect. Figure 4 demonstrates this effect for green Cu(H-sal-Ch)$_2$; its softly and coarsely ground powder shows Fig. 4(A), and, by further grinding the powder finely and forcefully, the spectrum changes to Fig. 4(B), in which a sharp absorption near 0.32 T remarkably increases in intensity relatively to other signals. It is interesting to note that this sharp signal completely agrees with Fig. 1(A) for its brown complex, indicating that polycrystals of green Cu(H-sal-Ch)$_2$ are transformed into those of the brown form by the grinding

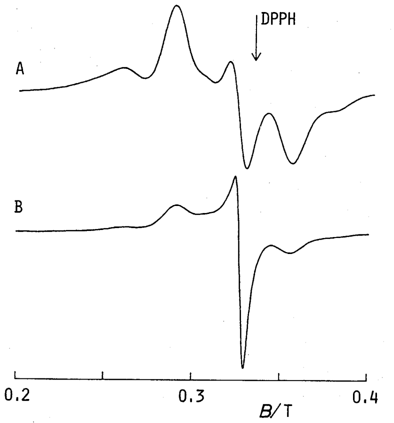

Fig. 4. Powder ESR spectra of green Cu(H-sal-Ch)$_2$ (X-band; room temperature): A, softly and coarsely ground powder; B, forcefully and finely ground powder.

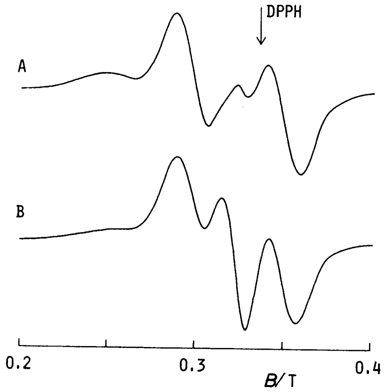

Fig. 5. Powder ESR spectra of green Cu(5-Cl-sal-Ch)$_2$ (X-band; room temperature): A, softly and coarsely ground powder; B, forcefully and finely ground powder.

effect. Roughly speaking, the grinding effect may be resolved into stress and frictional heat effects. Although heating the brown complex at 165—175 °C is known to yield the green one,[1,12] the brown complex showed no grinding effect. This fact suggests that the grinding effect is not always frictional heat effect, but may essentially be stress effect. The presumption that the brown form is favored by stress or pressure is also supported by the fact that the brown form of Cu(H-sal-Ch)$_2$ is slightly higher in density than the green one.[11] From a molecular-level point of view, the observation of the above grinding effect surprisingly means that a drastic molecular rearrangement from dimers to monomers, accompanied by molecular conformational changes, can take place easily in crystals without their melting.

Figure 5 shows another example of grinding effect for green Cu(5-Cl-sal-Ch)$_2$. Similarly, the green complex was transformed into the brown one by grinding effect. Green Cu(5-Cl-sal-Cp)$_2$ and green Cu(5-Br-sal-Cp)$_2$ showed spectral changes similar to those in Figs. 4 and 5, respectively, by grinding effect. A different spectral change due to the effect was also observed for olive brown Cu(5,6-benzo-sal-Ch)$_2$, as shown in Fig. 2. In this case, the grinding effect weakens the intensities of signals at both sides of the monomer's one, and slightly changes the monomer spectrum itself, suggesting that this complex possibly has two slightly different crystal forms. Judging from all these observations on the grinding effect, it is said that we must be careful of the possibility of the effect in any experiment where the grinding operation of crystals is needed.

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