ESR and Optical Absorption Studies of Various Bis(*N*-salicylidenealkylaminato)copper(II) Complexes with Tetrahedrally-distorted Coordination Geometry

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The ESR and visible absorption spectra of a number of bis(*N*-salicylidenealkylaminato)copper(II) complexes with different kinds of alkyl groups were measured in toluene. The coordinations of these complexes in toluene are distorted towards a tetrahedral geometry to varying extents; the relationship between the degree of the distortion and the ESR and visible absorption parameters was systematically investigated. Especially, the experimental fact that the absolute values of the hyperfine coupling constant with the copper nucleus decrease with an increase in the degree of distortion was discussed. A configurational equilibrium between two species with different degrees of the distortion was found to exist for the complexes with R=isopropyl and cyclohexyl in toluene.

A number of crystal structure determinations of bis(*N*-salicylidenealkylaminato)copper(II) complexes by three dimensional X-ray methods have been carried out,[1-6] and some of the complexes have been revealed to adopt tetrahedrally-distorted configurations in crystals, depending on the nature of the alkyl groups. Many other physicochemical measurements of these complexes in various states have been made in order to obtain some information about the stereochemistry and related properties.[7] There have been a few ESR reports on various copper(II) complexes with tetrahedral-coordination geometry.[8-10] It seems, however, that a satisfactory method for the precise interpretation of the ESR parameters of those complexes has not yet been established. In the present work, therefore, ESR and optical absorption studies of a series of bis(*N*-salicylidenealkylaminato)copper(II) complexes with many different kinds of alkyl groups, which are distorted towards a tetrahedral configuration to varying extents in solutions, have been carried out systematically.

Experimental

Materials. 11 kinds of bis(*N*-salicylidenealkylaminato)-copper(II) complexes were prepared and purified according to the usual method,[11] using commercial reagents; all the complexes are listed in Table 1, and hereafter they will be designated as Cu(*N*-R-sal)$_2$. Commercial toluene was purified by successive shaking with sulfuric acid and sodium hydroxide, followed by drying over sodium, and, finally, fractional distillation.

ESR and Visible Absorption Measurements. The ESR spectra of the above-mentioned complexes in toluene at a concentration of 1.0×10^{-2} mol/l were measured at room temperature and at the temperature of liquid nitrogen by means of a Hitachi 771 X-band ESR spectrometer. The visible absorption spectra of the complexes in toluene were recorded at room temperature on a Cary 14 spectrometer, using 1-cm quartz cells.

Results and Discussion

The crystal structures of the Cu(*N*-R-sal)$_2$ complexes with R=methyl,[1] *n*-propyl,[3] and *n*-butyl[5] are known to adopt normal planar configurations. On the other hand, X-ray analytical studies have revealed that the complexes with R=isopropyl[4] and *t*-butyl[6] in crystals are distorted towards a tetrahedral configuration because the alkyl groups are sufficiently bulky to prevent normal planar complexes from being formed. There is, however, an unexpected observation that Cu(*N*-ethyl-sal)$_2$ is distorted from planarity.[2] It appears, therefore, that intermolecular forces, *i.e.*, crystal packing forces, play an important and delicate role in determining the distortion. It is now unambiguous that the complexes with bulky alkyl groups in toluene are similarly distorted towards a tetrahedral configuration. The dipole-moment measurements of these complexes in dioxane and benzene suggest that this holds true.[12] This fact has also been supported by optical absorption spectral studies in such inert solvents as benzene and in various solid states.[12]

In this work, the visible absorption spectra were again measured at room temperature for all the present complexes in toluene in order to obtain systematic information about the coordination geometry; all the observed spectra are shown in Fig. 1. This figure indicates that the d-d spectra of the complexes appear

TABLE 1. ESR PARAMETERS[a] FOR Cu(*N*-R-sal)$_2$ IN TOLUENE

R	$g_{//}$	$g_{\perp}$[b]	$\lvert A_{//}\rvert$ $\times10^4$ cm^{-1}	g_0[c]	$\lvert A_0\rvert$[c] $\times10^4$ cm^{-1}
Methyl	2.217	2.055	195	2.109	76
Ethyl	2.221	2.055	186	2.110	74
n-Propyl	2.222	2.056	185	2.111	73
n-Butyl	2.223	2.055	184	2.111	73
n-Amyl	2.224	2.051	183	2.112	74
n-Hexyl	2.224	2.056	182	2.112	74
Isobutyl	2.222	2.057	181	2.112	73
Isopropyl	2.230		180	2.120	63
	2.253		156		
Cyclohexyl	2.230		180	2.117	65
	2.253		156		
s-Butyl	2.253	2.055	156	2.121	63
t-Butyl	2.270	2.068	145	2.135	43

a) Experimental errors in $g_{//}$ factor were ±0.001 and in $\lvert A_{//}\rvert$, ±1 (in the same unit as in the table), but those in g_0 and $\lvert A_0\rvert$ became somewhat large respectively, especially when the $\lvert A_0\rvert$ values were small. b) calculated from $g_0=(g_{//}+2g_{\perp})/3$. c) measured at room temperature.

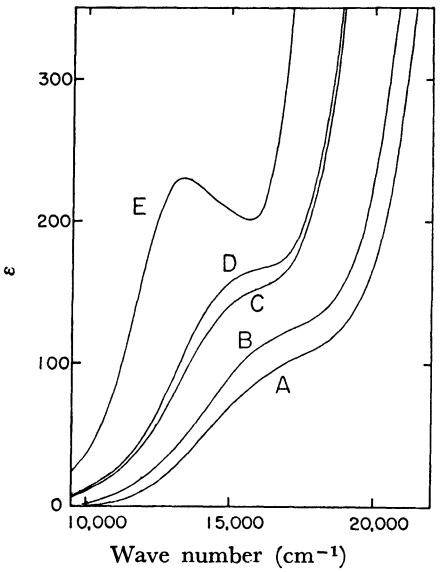

Fig. 1. Visible absorption spectra of the Cu(*N*-R-sal)$_2$ complexes in toluene at room temperature.
A: R=methyl. B: R=ethyl, *n*-propyl, *n*-butyl, isobutyl, *n*-amyl, and *n*-hexyl. C: R=cyclohexyl. D: R=isopropyl and *s*-butyl. E: R=*t*-butyl.

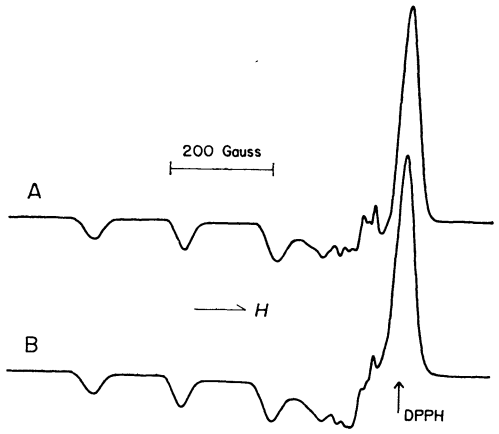

Fig. 2. X-band ESR spectra of the Cu(*N*-R-sal)$_2$ complexes with R=ethyl (A) and *n*-hexyl (B) in toluene at 77 K.

as shoulders on the longer-wavelength side of the near-ultraviolet intense bands, except for Cu(*N*-*t*-butyl-sal)$_2$, whose d-d spectrum appears only as a peak. It is difficult, therefore, to discuss these d-d spectra in detail. Two important observations, however, can be made in Fig. 1. One is the tendency for the intensities of the d-d spectra to increase in the spectral order of I to V, while the d-d spectra shift to longer wavelengths in the same spectral order. This tendency is consistent with the dependence of the spectral change on a distortion of the coordination geometry towards tetrahedron.[13,14] The other is the fact that the Cu(*N*-R-sal)$_2$ complexes with R=ethyl, *n*-propyl, *n*-butyl, isobutyl, *n*-amyl, and *n*-hexyl exhibit almost the same spectra, while the d-d spectra of the complexes with *R*=α-branched alkyl (*s*-alkyl) groups, *i,e.*, isopropyl, *s*-butyl, *t*-butyl, and cyclohexyl, become more intense than those of the R=α-non-branched alkyl groups.

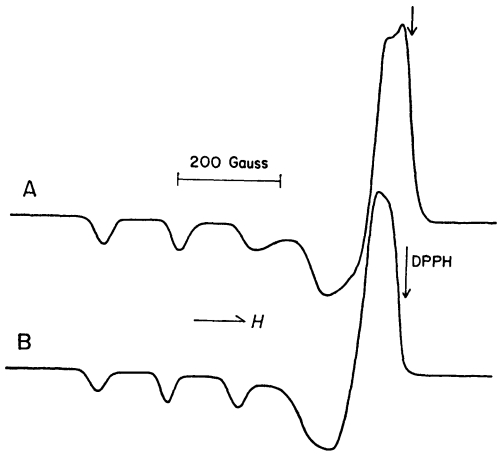

Fig. 3. X-band ESR spectra of the Cu(*N*-R-sal)$_2$ complexes with R=*s*-butyl (A) and *t*-butyl (B) in toluene at 77 K.

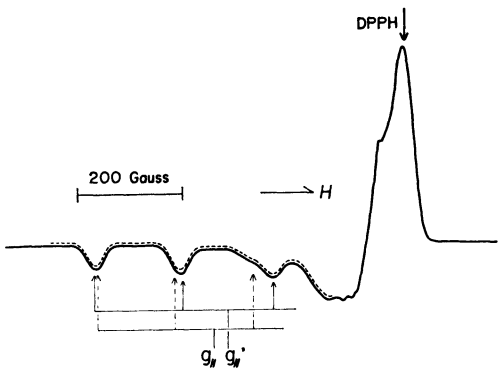

Fig. 4. X-band ESR spectrum of Cu(*N*-isopropyl-sal)$_2$ in toluene at 77 K (see the text as to the dotted line, $g_{\parallel}$, and $g_{\parallel}'$ written in the figure).

A similar classification of the Cu(*N*-R-sal)$_2$ complexes could also be made on the basis of ESR results. The ESR spectra of the complexes with R=ethyl, *n*-propyl, *n*-butyl, isobutyl, *n*-amyl, and *n*-hexyl were similar to one another; two of them are shown in Fig. 2. Cu(*N*-methyl-sal)$_2$, however, was different from the above-mentioned group of complexes in that its ESR spectrum was made up by the superposition of a spectrum due to those mentioned above and of a spectrum due to a triplet-state dimer.[15] On the other hand, the ESR spectra of the complexes with R=*s*-butyl, *t*-butyl, isopropyl, and cyclohexyl, the former three of which are shown in Figs. 3 and 4, were quite different in line shape from those in Fig. 2; the spectrum of the last complex was similar to the one in Fig. 4. The spectra in Fig. 3 are different in both line width and line position from those in Fig. 2. A detailed discussion of Fig. 4 will be given later. All the ESR parameters, which are listed in Table 1, were determined on the assumption that all the *g* and *A* tensors are of an axial or nearly axial symmetry. This assumption is supported by the experimental fact that the ESR spectra in Fig. 3 are of an axial type of line shape.

The expressions for the principal values of *g* and *A* tensors in terms of the coefficients in one-electron LCAO MOs have already been given in detail for the copper-

(II) complexes, whose coordination around the metal ion is a flattened tetrahedron.[8,9] It has been revealed experimentally and theoretically that, for each of the complexes, the $g_{//}$ value increases with an increase in the degree of the distortion towards a tetrahedral coordination geometry, and that there is a slight increase in the $g_{\perp}$ value (or g_x and g_y) up to the limit of a small degree of distortion.[10] It can, furthermore, be reasonably estimated from the equation of $A_{//}$ that the $|A_{//}|$ value also decreases with an increase in the degree of the distortion, since then the increases in both the $g_{//}$ value and the square value of the mixing coefficient of the 4p atomic orbital in the equation effectively contribute to a decrease in the $|A_{//}|$ value.[8,9]

The ESR data listed in Table 1 clearly indicate that the $g_{//}$ values of the Cu(*N*-R-sal)$_2$ complexes with R= methyl, ethyl, *n*-propyl, *n*-butyl, *n*-amyl, and *n*-hexyl increase slightly in this order of complexes, and that the $|A_{//}|$ values also decrease slightly in the same order. It is obvious that Cu(*N*-isobutyl-sal)$_2$ also belongs to this group. In this order of complexes, however, the two neighbors between which the largest differences in the $g_{//}$ and $|A_{//}|$ values were detected are the complexes of R=methyl and ethyl, as may be seen in the table. This fact, combined with the visible absorption spectral results shown in Fig. 1 and the crystal structural result that even Cu(*N*-ethyl-sal)$_2$ can adopt a tetrahedrally-distorted configuration,[2] suggest that all the complexes of this group except Cu(*N*-methyl-sal)$_2$ may have similar structures, with a slight distortion towards tetrahedral coordination geometry in toluene. On the other hand, the $g_{//}$ values of the complexes with R=*s*-butyl and *t*-butyl are remarkably large, and their $|A_{//}|$ values are remarkably small, compared with those of the above-mentioned group of complexes. This fact, combined with the visible absorption spectral results and the crystal structural results for Cu(*N*-*t*-butyl-sal)$_2$, indicates that the coordination geometry of these two complexes in toluene is highly distorted towards tetrahedron.

It is a noteworthy experimental fact that the $|A_0|$ values of the complexes with R=α-branched alkyl groups become considerably smaller than those of the complexes with R=α-non-branched alkyl groups, as is shown in Table 1. For Cu(*N*-*t*-butyl-sal)$_2$, furthermore, the decrease in the $|A_0|$ value was found to be comparable in magnitude to that in the $|A_{//}|$ value. A_0 is written in terms of the Fermi contact term for the free ion, κ, by this relation:[8,9]

$$A_0 = -(P_d a^2 + P_p b^2),$$

where $P_{d,p}=2\gamma\mu_0\mu_N\langle r^{-3}\rangle_{3d,4p}$, μ_N being the nuclear magneton and γ being the nuclear gyromagnetic ratio, and where a and b are the mixing coefficients of the 3d and 4p atomic orbitals in the ground-state unpaired-electron molecular orbital. One has $P_d : P_p = 828.7 : (925\pm40)$[8,9] and $P_d = 0.036$ cm^{-1}.[16] The equation of A_0 states that A_0 is almost independent of any distortion towards a tetrahedral configuration. The above-mentioned experimental fact, therefore, is clearly in conflict with an estimation derived from this equation. Freeman and Watson have revealed, through an unrestricted Hartree-Fock calculation of the spin-polarization of the 4s electrons by an exchange interaction with the 3d unpaired electron for a copper atom in the $3d^94s^2$ configuration, that the spin-polarization of the 4s electrons contributes to a weakening of the isotropic Fermi contact interaction.[17,18] The small $|A_0|$ values of the complexes with R=*s*-butyl and *t*-butyl, therefore, can be interpreted in terms of an increase in the electron density on the 4s orbital with an increase in the degree of distortion. This interpretation is plausible in view of the fact that the charge neutralization on the metal ion is facilitated by electron donation from the ligand orbitals to the metal 4s orbital, rather than by that to the metal 3d orbital, because the interaction between the ligand and 3d orbitals is weakened by the tetrahedral distortion. On the basis of this interpretation, the degree of decrease in the $|A_0|$ value would give a measure of the electron density on the metal 4s orbital. The possibility that there may be another mechanism of decrease in the $|A_0|$ value, however, can not be excluded, because there has been no information about the spin-polarization of all the s-electrons caused by an exchange interaction with the metal 4p unpaired electron inevitably produced in the unpaired-electron molecular orbital.

The dipole moments of a number of the Cu(*N*-R-sal)$_2$ complexes have been measured in dioxane and benzene.[13,7] The results have revealed that the complexes of R=isopropyl and *t*-butyl do have substantial permanent dipole moments, and that the values increase in this order: *n*-propyl$\sim$*n*-butyl<isopropyl$\sim$*s*-butyl<*t*-butyl. These data, however, do not distinguish between a configurational equilibrium as is found for many nickel(II) complexes[7] and the existence of a single structural species. The ESR spectrum of Cu(*N*-isopropyl-sal)$_2$ in toluene, which is shown in Fig. 4, is different in line shape from the types of spectra in both Figs. 2 and 3. The dotted line in the low-field part of Fig. 4 is a spectrum simulated according to the superposition of the types of spectra in both Figs. 2 and 3 with $g_{//}'$ and $g_{//}$ at the intensity ratio of 3 to 2; actually, the spectrum of Fig. 3(A) itself was utilized for the spectral simulation. The dotted-line spectrum is in satisfactory agreement with the observed one, especially at the part of the hyperfine absorption lines of $I_z=1/2$, as may be seen in Fig. 4. Thus, we may conclude that a configurational equilibrium between two complex species with different degrees of the tetrahedral distortion exists for this complex in toluene. Such is also the case with Cu(*N*-cyclohexyl-sal)$_2$, since this complex showed an ESR spectrum analogous to that of Cu(*N*-isopropyl-sal)$_2$. On the other hand, the ESR line shapes shown in Fig. 3 suggest that the complexes of R=*t*-butyl and *s*-butyl may be dissolved as a single structural species in toluene.

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