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The ESR Spectra of Bis(*t*-butyl and ethyl acetoacetato)copper(II) Complexes in Various Hydrocarbon Solvents

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Synopsis. The X-band ESR spectra of bis(*t*-butyl acetoacetato)copper(II) and bis(ethyl acetoacetato)copper(II) in several non-coordinating solvents of hydrocarbon were measured at 77 K. Remarkable solvent effects on dimer formation were revealed for the complexes.

Recently, it has been revealed through ESR investigations that various copper(II) chelates of β-diketones, N-alkylsalicylaldimines, and related compounds are dimerized into triplet-state dimers to varying extents in toluene and chloroform.[1-5] However, there are many points to be clarified as to the factors on which the dimer formation depends. It is the purpose of this paper to investigate the solvent effects on such dimer formation using various hydrocarbon liquids as non-coordinating solvents.

Experimental

The copper(II) chelates employed here are bis(*t*-butyl acetoacetato)copper(II) and bis(ethyl acetoacetato)copper(II) (hereinafter abbreviated as Cu(*t*-Buoac)$_2$ and Cu(Etoac)$_2$ respectively). They were prepared and purified according to the usual method.[6] The chelate reagents were commercially available. The solvents used were ethylbenzene, toluene, methylcyclohexane, and 2-methylpentane, all of which were purchased as G. R. grade reagents. The first three solvents were further purified by succesive shaking with sulfuric acid and sodium hydroxide, followed by drying over sodium and, finally, fractional distillation. The methylcyclohexane was also passed through a column packed with silica gel. The ESR spectra were recorded at the temperature of liquid nitrogen over the field range of 0 to 6000 G by means of a Hitachi 771 X-band ESR spectrometer. All the sample solutions used for the ESR measurements were in the concentration of 1.0×10^{-2} M. The approximate solubilities of the Cu(*t*-Buoac)$_2$ in the solvents were determined at room temperature by the usual spectrophotometric method.

Results and Discussion

The ESR spectra of Cu(*t*-Buoac)$_2$ in the three solvents, toluene, methylcyclohexane, and 2-methylpentane, are shown in Fig. 1. The spectrum in ethylbenzene was analogous in line shape to that in toluene. The (A) spectrum in Fig. 1 is a typical one for mononuclear copper(II) complexes in a magnetically-diluted polycrystalline state.[7] On the other hand, it is clear that both the (B) and (C) spectra in the figure are made up of the superposition of a monomer spectrum quite similar to the (A) spectrum and a triplet-state spectrum resulting from dimers: this is quite analogous to the situation previously reported for Cu(Etoac)$_2$ in toluene.[1] Accordingly, it may be concluded that Cu(*t*-Buoac)$_2$ also is dissolved in methylcyclohexane and 2-methylpentane in the form of the monomeric and dimeric species which are at equilibrium ($2M \rightleftharpoons M_2$). Moreover, both of the triplet-state ESR spectra observed for Cu(*t*-Buoac)$_2$ in this work and for Cu(Etoac)$_2$ in toluene are quite similar in line shape.

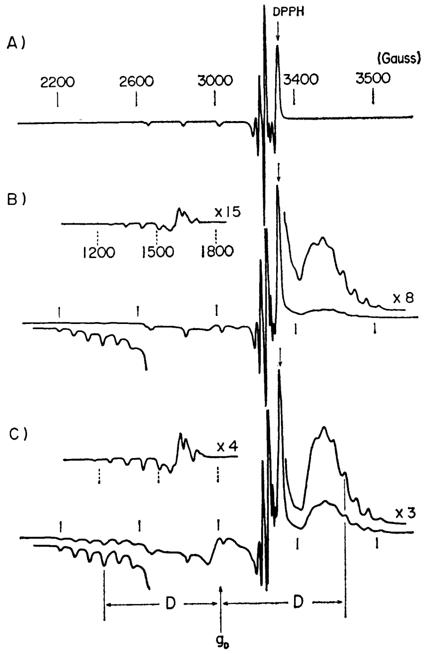

Fig. 1. The X-band ESR spectra of bis(*t*-butyl acetoacetato)copper(II) at 77 K in the following solvent at a concentration of 1.0×10^{-2} M.
(A): toluene, (B): methylcyclohexane, (C): 2-methylpentane.

The large absorption line observed at the highest field in Fig. 1 (A) is due to the extra-hyperfine structure of $M_I=3/2$.[8] As this figure shows, accordingly, this complex in toluene has nearly tetragonal g and A tensors. The magnetic parameters for the monomers of (A) in Fig. 1 were as follows; $g_{//}=2.270$, $g_{\perp}=2.052$, $|A_{//}|=192\times10^{-4}$ cm^{-1}, and $|A_{\perp}|=25\times10^{-4}$ cm^{-1}. On the other hand, the parameters for the triplet-state dimers of (B) and (C) in Fig. 1, g_D and D, which are defined in Fig. 1 (C), were as follows; $g_D=2.185$ and $D=623\times10^{-4}$ cm^{-1}. The copper-copper distance in the dimers, R, could then be estimated to be 3.65 Å from the equation of $R=(0.650\,g_D/D)^{1/3}$, using the above-determined g_D and D values.[1-3] These g_D, D, and R values are also close to those for the dimers of Cu(Etoac)$_2$ in toluene.[1] Therefore, the two dimeric structures seem to be almost the same; in these dimers, monomeric halves are situated with parallel planes, and the directly-coordinating oxygen atoms of adjacent molecules occupy the apical positions of the copper atom.[1]

Figure 1 indicates that there are remarkable solvent effects on the dimer formation for these kinds of copper(II) complexes; that is, the equilibrium constant, K, of $2M \rightleftharpoons M_2$ is largely dependent upon the property of the solvents. The K value for Cu(t-Buoac)$_2$ in toluene is close to zero, as has been described above. On the other hand, the K value for the complex in methylcyclohexane is quite small compared with that in 2-methylpentane, since it is clear that the ratio of the intensity of triplet-state ESR signals to that of doublet-state ones in (B) is smaller than that in (C).[1] Thus, the K values increase remarkably in this order: toluene<methylcyclohexane<2-methylpentane. On the other hand, the dielectric constants decrease in the same order: toluene(2.38)>methylcyclohexane(2.02)>2-methylpentane (1.88).[9] Moreover, it was found that the solubilities of the complex also decrease in the same order: toluene (1.30 M)>methylcyclohexane (0.37 M)>2-methylpentane (0.26 M), where the concentrations written in parentheses express the approximate concentrations of saturated solutions at room temperature. These facts suggest that the solubility of a complex in a solvent becomes smaller as the dielectric constant of the solvent decreases and, furthermore, that the complex tends to be dissolved in a solvent with a low dielectric constant in the form of dimers rather than in the form of monomers.

There seems to be no significant difference in property between toluene and ethylbenzene.[9] The ESR spectra of Cu(Etoac)$_2$ in both of the solvents are shown in Fig. 2. These two spectra are different in line shape, especially over the field range of 3100 to 3400 G. However, since their half-field ESR spectra for $\Delta M=2$ transitions are almost the same, there is no doubt that the same triplet-state dimers are formed in both solutions. Accordingly, it can be expected from the line shape of (B) that, in this solution, there exists another species, which may possibly be a polymer, besides the dimer and monomer species. In any event, it is obvious from Figs. 1 and 2 that the dimer formation for these kinds of copper(II) complexes is susceptible to a slight difference in the properties of the solvents.

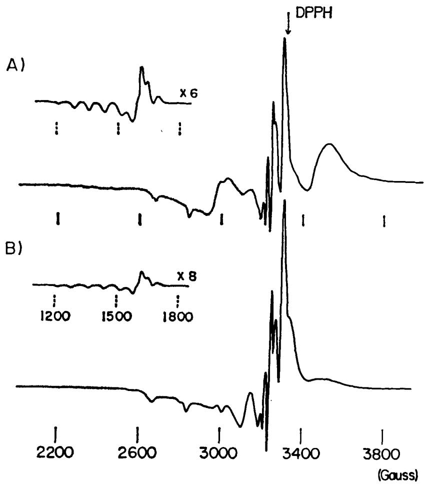

Fig. 2. The X-band ESR spectra of bis(ethyl acetoacetato)copper(II) at 77 K in the following solvents at a concentration of 1.0×10^{-2} M.
(A): toluene, (B): ethylbenzene.

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