CHEMISTRY LETTERS, pp. 1023-1026, 1973. Published by the Chemical Society of Japan

THE NEW TRIPLET-STATE DIMERS FORMED BY MIXING BIS(N-ALKYLSALICYLALDIMINATO)COPPER(II) WITH CERTAIN BIS(β-DIKETONATO)-COPPER(II) COMPLEXES IN TOLUENE

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ESR experiments have revealed that bis(N-alkylsalicylaldiminato)-copper(II) forms a new kind of triplet-state dimer in toluene with certain bis(β-diketonato)copper(II) complexes such as bis(hexafluoroacetylacetonato)copper(II), bis(1,1,1-trifluoroacetylacetonato)-copper(II), etc.

The properties of the mixed-ligand complexes of CuAB-type in various solvents have been systematically investigated by ESR and optical absorption techniques using about 20 kinds of β-diketones and related compounds as A and B,$^{1)}$ where CuAB has been formed in the solutions according to the equilibrium of $CuA_2 + CuB_2 \rightleftarrows 2\ CuAB$. We obtained the new finding that only the equilibrium systems of A = N-alkylsalicylaldiminate and B = fluorinated β-diketonate in toluene unusually show strong triplet-state ESR signals; this fact indicates that new kinds of triplet-state dimers are formed in high concentrations only in these systems. This communication reports this ESR result.

The complexes employed here are $Cu(nps)_2$, $Cu(nms)_2$, $Cu(hfac)_2$, $Cu(tfac)_2$, $Cu(bfa)_2$, $Cu(bzac)_2$, and $Cu(dpm)_2$, where nps, nms, hfac, tfac, bfa, bzac, and dpm stand for the anions of N-n-propylsalicylaldimine, N-methylsalicylaldimine, hexafluoroacetylacetone, 1,1,1-trifluoroacetylacetone, 3-benzoyl-1,1,1-trifluoroacetone, benzoylacetone, and dipivaloylmethane, respectively. The 1.00×10^{-2} M toluene solutions of the complexes and their mixtures were used as sample solutions for ESR measurements. ESR spectra were recorded over the field range of 0 to 6,000 gauss at the temperature of liquid nitrogen with a Hitachi 771 X-band spectrometer.

The ESR spectra of $Cu(hfac)_2$, $Cu(nps)_2$, and the equimolar mixture of them are shown in Fig. 1. This figure makes us suspect that the mixture shows no ESR signals. The ESR spectrum of (A) in Fig. 1 is the typical one for the monomeric copper(II) complexes.$^{2)}$ The main species of $Cu(nps)_2$ in toluene also is monomer, as judged from its ESR line shape ((B) in Fig. 1), although dimer formation in the toluene solution takes place to a slight extent for this complex.$^{3)}$ By adding either of the parent complexes in a slight excess, the ESR spectrum of (C) in Fig. 1 was changed into the one made up of the superposition of the (C) spectrum and the monomer spectrum due to the excess parent complex. When ESR signals were highly amplified, however, the 1:1 mixture of $Cu(nps)_2$ and $Cu(hfac)_2$ in toluene was found to

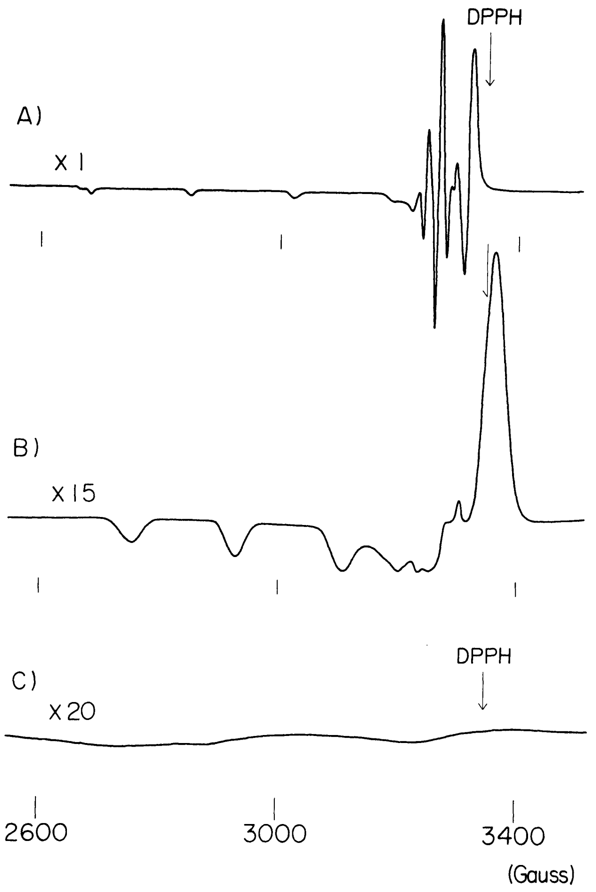

Fig. 1. X-band ESR spectra at 77°K (the number written at the left-hand side of each spectrum expresses its relative amplification degree).

(A) the 1.00 X 10^{-2} M toluene solution of $Cu(hfac)_2$, (B) the 1.00 X 10^{-2} M toluene solution of $Cu(nps)_2$, (C) the equivolume mixture of the (A) and (B) solutions.

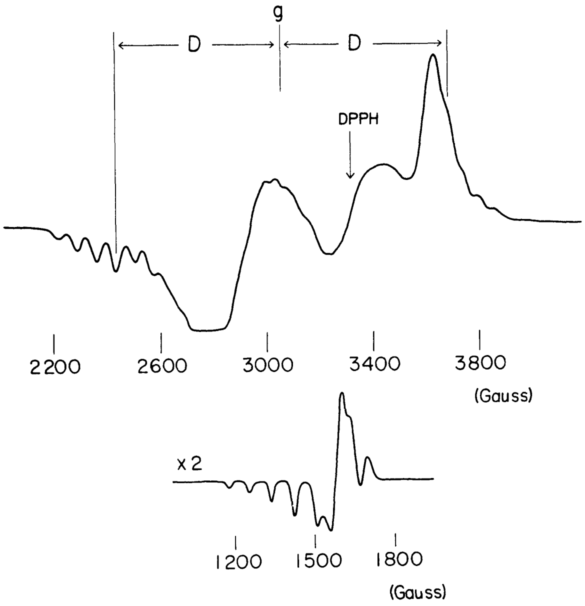

Fig. 2. The highly amplified ESR spectrum of (C) in Fig. 1.

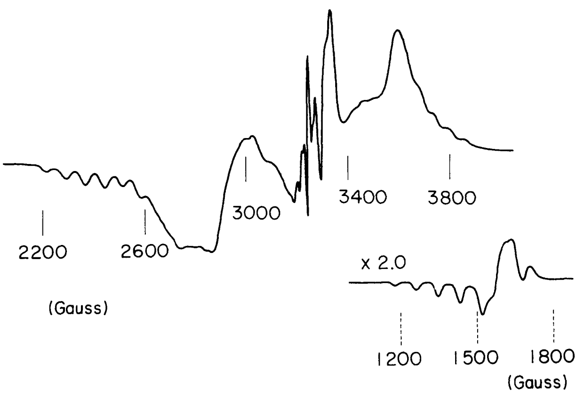

Fig. 3. The X-band ESR spectrum of the equivolume mixture of the 1.00 X 10^{-2} M toluene solutions of $Cu(nps)_2$ and $Cu(tfac)_2$ at 77°K.

show a typical ESR signal of the triplet-state dimers of copper(II), as is shown in Fig. 2. It is thought, therefore, that the two parent complexes react at 1 to 1 ratio to form triplet-state dimers in toluene. The mixture of Cu(hfac)$_2$ and Cu(nms)$_2$ also showed the same ESR results in toluene, in spite of the fact that Cu(nms)$_2$ is dimerized into dimers in toluene to a larger extent than Cu(nps)$_2$.$^{3)}$

For Cu(tfac)$_2$ as well as for Cu(hfac)$_2$, dimer formation in toluene does not take place.$^{1,\ 4)}$ The ESR spectrum of the equimolar mixture of Cu(nps)$_2$ and Cu(tfac)$_2$, which was different in line shape from that shown in Fig. 2, is shown in Fig. 3. This spectrum is made up of the superposition of the three different spectra, one of which is the same triplet-state spectrum as mentioned above and the other two of which are those due to the two parent complexes. In Fig. 3, however, the integrated intensity of the dimer spectrum is extremely strong compared with those of the monomer spectra; in this system also the main species in the solution is triplet-state dimer. Such was the case with the mixture of Cu(nps)$_2$ and Cu(bfa)$_2$. It is of interest that the triplet-state ESR spectra of the same type could not be observed for the mixtures of Cu(nps)$_2$ and Cu(bzac)$_2$ and of Cu(nps)$_2$ and Cu(dpm)$_2$. The fact that Cu(nps)$_2$ reacts with the complexes with fluorinated β-diketones to form such dimers as mentioned above suggests that the electronic factors of the parent complexes play an important role in such dimer formation rather than the steric ones.

The ESR line shapes of the triplet-state dimers of copper(II) have been investigated by several authors.$^{5,\ 6)}$ The data given by them, however, are insufficient to analyze the present complicated ESR spectra exactly, although we can recognize that these spectra for $\Delta M = 1$ transitions have some similarity in line shape to the previously reported ones for Cu(nms)$_2$ and bis(ethyl acetoacetato)copper(II) (hereinafter abbreviated as Cu(etacest)$_2$) in toluene.$^{6,\ 7)}$ On the other hand, however, only the copper-copper distance, r, in the dimers can be estimated with considerable accuracy from the following equation: $r = (0.650\ g^2/D)^{1/3}$, where g and D are defined in Fig. 2. The determined g and D values are listed in Table 1, together with the estimated r values. Any of the parameters in the table are almost the same for all

TABLE 1. MAGNETIC PARAMETERS AND ESTIMATED r VALUES

Dimer$^{a)}$	g	D (cm^{-1})	r (Å)
Cu(nps)$_2$ + Cu(hfac)$_2$	2.169	0.0632	3.64
Cu(nms)$_2$ + Cu(hfac)$_2$	2.169	0.0642	3.63
Cu(nps)$_2$ + Cu(tfac)$_2$	2.164	0.0627	3.65
Cu(nps)$_2$ + Cu(bfa)$_2$	2.167	0.0629	3.65

a) Dimers correspond to those formed from the two parent complexes written in this column.

the dimers. This fact means that all the dimeric structures are of the same type. Interestingly, the r values thus estimated are close to those of $Cu(nms)_2$ and $Cu(etacest)_2$.[6, 7] Thus it seems probable that the present dimers are similar in structure to those of $Cu(nms)_2$ and $Cu(etacest)_2$.

All the experimental facts above-mentioned suggests that the dimers under discussion are formed by the dimerization of the mixed-ligand complexes, CuAB, in toluene. It may be expected, accordingly, that the following equilibriums are established in the present solutions:

$$CuA_2 + CuB_2 \xrightleftharpoons{K_M} 2\ CuAB \xrightleftharpoons{K_D} (CuAB)_2$$

The K_D value of the equilibrium system with $Cu(nps)_2$ and $Cu(hfac)_2$ is especially large, because no ESR signals could not be observed except that due to the dimers. There must be, accordingly, some strong driving forces by which such a dimer formation is promoted. It is difficult, however, to estimate the exact structure of $(CuAB)_2$ at present. Further works on these problems are now in progress.

The author is grateful to Prof. T. Isobe for his encouragement throughout this work, and he also wishes to thank Mr. M. Otagiri, Nagoya City University, for his valuable advice.

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(Received July 3, 1973)