BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 447—451 (1973)

ESR Studies of Dimer Formation by the β-Diketone Chelate Complexes of Copper(II) in Toluene[1)]

Hiroshi Yokoi and Taro Isobe

Chemical Research Institute of Non-aqueous Solutions, Tohoku University, Katahira, Sendai

(Received January 6, 1972)

A study of the ESR spectra of several β-diketone chelate complexes of copper(II) in the frozen solution of toluene has revealed that triplet-state dimers are formed at high concentrations in the solution and that these dimers are in equilibrium with only the monomers. The approximate equilibrium constants have been determined by a careful analysis of the ESR spectra observed in various concentrations. Structures for the dimers have been suggested from magnetic parameters properly determined using a point dipole model.

In recent years, many ESR studies of the triplet state of binuclear copper(II) complexes have been carried out with especial interest being taken in the mechanisms of the magnetic interactions between the two copper atoms.[2-11)] There have, however, been only a few ESR investigations of the triplet state obtained by the dimerization of mononuclear stable copper(II) complexes.[12-14)] The ESR experiments described in this paper will establish the new fact that dimeric and

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monomeric species coexist at equilibrium in the toluene solutions of some copper(II) β-diketonates. The purpose of this paper is to propose structures for the dimers and to determine the equilibrium constants through an analysis of the observed ESR spectra.

Experimental

Materials. The β-diketone chelate complexes of copper(II) employed in this work are $Cu(acac)_2$, $Cu(bzac)_2$, $Cu(Etacest)_2$, and $Cu(Meacest)_2$, where acac, bzac, Etacest, and Meacest are the anions of acetylacetone, benzoylacetone, ethyl acetoacetate, and methyl acetoacetate respectively. They were prepared and purified according to the usual method.[15] Commercial toluene was purified by successive shaking with sulfuric acid and sodium hydroxide, followed by drying over sodium and, finally, fractional distillation.

ESR Measurements. The ESR spectra of the above-mentioned complexes in toluene in various concentrations were measured at the temperature of liquid nitrogen over the field range of 0 to 6,000 gauss, using a Hitachi 771 X-band ESR spectrometer. The toluene solutions were transferred into quartz tubes 4 mm in internal diameter and then solidified with liquid nitrogen as quickly as possible. These frozen solutions were the actual samples for ESR measurements used in this work.

Results and Discussion

The observed ESR spectra of $Cu(Etacest)_2$ and $Cu(acac)_2$ in toluene at the temperature of liquid nitrogen are shown in Figs. 1 and 2 respectively. $Cu(Meacest)_2$ and $Cu(bzac)_2$ were similar to $Cu(Etacest)_2$ and $Cu(acac)_2$ respectively in the ESR line shape. These spectra are complicated, and all of them showed weak absorptions at the low-field of about 1,500 gauss. The ESR spectra in these figures which are constructed by excluding sharp absorption lines are similar in line shape to the spectra observed for various binuclear copper(II)

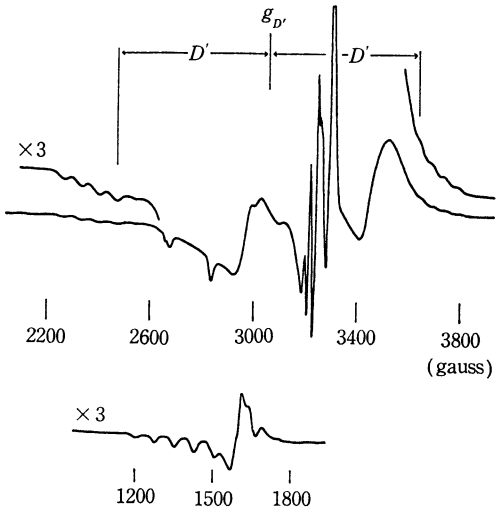

Fig. 1. The X-band first-derivative ESR spectrum of $Cu(Etacest)_2$ in toluene at 77K (c^0 : 1.03×10^{-2} M, the lower spectrum is the half-field spectrum of the $\Delta M=2$ transition).

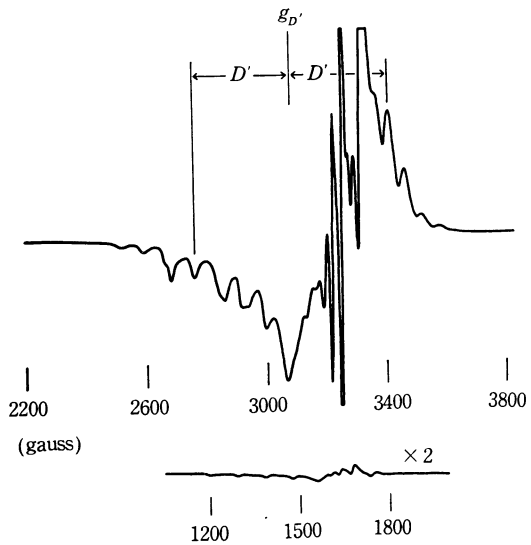

Fig. 2. The X-band first-derivative ESR spectrum of $Cu(acac)_2$ in toluene at 77K (c^0 : 2.22×10^{-3} M).

complexes with copper-copper spin interactions.[5-14] The ESR line shapes for randomly-oriented and magnetically-diluted copper(II) complexes have been studied in some detail by many investigators.[16] It can be clearly understood by a comparison of all these ESR line shapes that all the ESR spectra observed in this work are made up to the superposition of two types of spectra; one is due to triplet-state dimers, and the other, due to doublet-state monomers.

The spin Hamiltonian for triplet-state copper(II) dimers, on the assumption of axial symmetry, is written as follows:

$$H = \beta[g_{//}H_zS_z+g_\perp(H_xS_x+H_yS_y)] + D[S_z^2-S(S+1)/3] + A_{//}S_zI_z + A_\perp(S_xI_x+S_yI_y) \quad (1)$$

where all the symbols have their usual meanings. The zero-field splitting parameter, D, is composed of the following two terms:

$$D = D_{dd} + D_{pseudo} \quad (2)$$

In Eq. (2), D_{dd} expresses the magnetic dipole-dipole interaction term, and $D_{pseudo}=-J[(g_{//}-2)^2/4-(g_\perp-2)^2]/8$, where $-J$ is the energy separation between the singlet ground state and the first excited triplet state.[2] We wish now to estimate D_{dd}, from which the copper-copper atomic distance, R, can be estimated; then, the structures for the corresponding dimers can be proposed.[9,17] Since D only is a measurable value, D_{pseudo} must be estimated in order to determine D_{dd}. It has been considered that the structures for dimeric complexes in solution may be analogous to those in a crystal and that the $-J$ values in the two states may be almost the same.[14] The $-J$ value of $Cu(acac)_2$ in a crystal has been estimated to be less than 0.3 cm^{-1} from the value of θ in the

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Curie-Weiss formula[18,19] and from the unification phenomenon of two separate ESR absorption lines with different g values due to a spin-exchange interaction.[20] The value of D_{pseudo} for $Cu(acac)_2$ in a crystal, which can be calculated from the above-described equation of D_{pseudo} using the above-estimated $-J$ value, is no more than a small percentage of the experimentally-determined D values (about 0.05 cm^{-1}) in this work. Furthermore, a change in the $-J$ value does not sensitively contribute to the calculated R value.[10] The assumption of $D=D_{dd}$, therefore, holds approximately good for all the dimers in this work. The copper-copper atomic distance, R, can be approximately estimated by means of the following equation, derived by the use of a point dipole model:

$$R = (0.650\, g_{//}^2/D_{dd})^{1/3} \quad (3)$$

where $g_{//}$ and D_{dd} are the parameters defined in Eqs. (1) and (2).[9,17] It has been demonstrated that the agreement between the experimentally-determined R value and the R value estimated from Eq. (3) is fairly good.[10] A closer examination of the ESR spectra observed in this work shows that the hyperfine coupling constants observed at the two edges of the triplet spectra for $\Delta M=1$ are appreciably different from each other. Chikira and Isobe have revealed, through the computer simulation of these types of triplet ESR line shapes, that the above-mentioned differences in the hyperfine structure are due to the discrepancy between the principal axes of the D and A tensors in orientation.[21] They have also reported that, generally, the approximate R value can be obtained directly by substituting $g_{D'}$ and D' for $g_{//}$ and D_{dd} respectively in Eq. (3), regardless of the $-J$ value over a considerable wide range, where $g_{D'}$, and D' are defined in Figs. 1 and 2.[21] The analyzed results for all the complexes are listed in Table 1.

The first two complexes in Table 1 are quite similar to each other in ESR behavior; such is also the case with the other two complexes in the table. The molecular configuration of $Cu(acac)_2$ in a crystal is schematically shown in Fig. 3(A), where the R value

Table 1. Magnetic parameters and R[a] values

Copper(II) complex	Monomers			Dimers		
	$g_{//}$	$g_{\perp}$	$\lvert A_{//}\rvert$ $\times 10^4$ cm^{-1}	$g_{D'}$[b]	D'[b] $\times 10^4$ cm^{-1}	R (Å)
$Cu(Etacest)_2$	2.282	2.05	176	2.174	590	3.73
$Cu(Meacest)_2$	2.275	2.06	174	2.167	581	3.75
$Cu(acac)_2$	2.255	2.05	191	2.161	326	4.53
$Cu(bzac)_2$	2.255	2.05	192	2.157	331	4.50

a) R represents the copper-copper distance (Å).
b) The parameters are defined in Figs. 1 and 2.

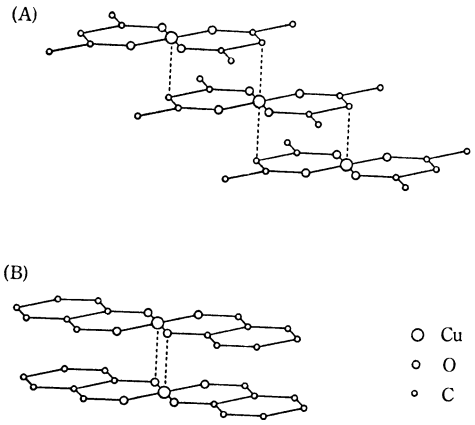

Fig. 3. The schematically represented crystal structures of (A): $Cu(acac)_2$ and (B): crystal form of bis-(salicylaldehydato)copper(II).

is 4.52 Å.[22] This R value surprisingly agrees with the R value calculated from D' value, as is shown in Table 1. Accordingly, it may be concluded that the dimeric structure of $Cu(acac)_2$ in toluene is the same as that in a crystal and that, furthermore, the dimers of $Cu(bzac)_2$ in toluene also have a similar structure. On the other hand, the crystal structure of $Cu(Etacest)_2$, whose R value is 4.53 Å,[23] is analogous to that of $Cu(acac)_2$; in their crystals, the carbon atoms of the –CH– groups of adjacent molecules occupy the apical positions of the copper atom. The R value calculated from D' for the dimers of $Cu(Etacest)_2$ in toluene is 3.75 Å, as is listed in Table 1. The large difference between the two R values for this complex clearly indicates that its dimeric structure in toluene is quite different from that in a crystal. Interestingly, (salicylaldehydato)copper(II), which is analogous in physical and chemical behavior to $Cu(Etacest)_2$,[26,27] has two different crystal structures[24,25]; one is similar to the crystal structure of $Cu(acac)_2$, and the other, to those of N,N'-disalicylidene ethylenediamine copper(II),[28] the γ-form of bis-(N-methyl-salicylaldiminato)copper(II),[29] and bis-(8-hydroxyquinolinato)copper(II).[30] The latter crystal structure is schematically shown in Fig. 3(B), where the directly-coordinating oxygen atoms of adjacent molecules occupy the apical positions of the copper atom. The R value is calculated to be 3.73 Å for this type of structure, assuming about 3.15 Å as a reasonable copper-apical oxygen distance. It seems likely, therefore, that the

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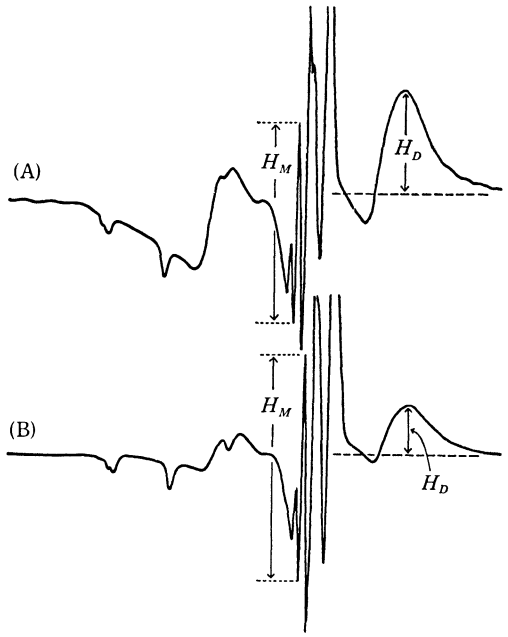

Fig. 4. The concentration dependence of the first-derivative ESR spectra of Cu(Etacest)$_2$ in toluene at 77K.
(A): $c^0=1.03\times10^{-2}$ M, (B): $c^0=0.23\times10^{-2}$ M.

dimers of Cu(Etacest)$_2$ in toluene have a structure analogous to the one shown in Fig. 3(B).

A large concentration dependece of the ESR spectra was observed for each of the complexes employed here, as is shown in Fig. 4. The Q value can now be defined as the intensity ratio of a certain absorption line of the dimers to a certain line of the monomers in a first-derivative ESR spectrum; for instance, $Q=H_D/H_M$ in the case of Fig. 4. It is clear that all the complexes in toluene regularly change in their Q values with their initial concentrations, as may be seen in Fig. 4. It seemed that it would be very interesting to see whether or not the following type of equilibrium is established in the solution:

$$2M \rightleftharpoons M_2 \tag{4}$$

$$K=\frac{[M_2]}{[M]^2} \tag{5}$$

where M and M_2 represent monomeric and dimeric molecules respectively. An attempt to establish the proof of the presence of such an equilibrium and to determine the K value will be described below.

When q is introduced as the proportional constant of the equation $Q=q\cdot([M_2]/[M])$, the following equation can be derived from Eq. (5):

$$2Q^2+qQ=Kq^2c^0 \tag{6}$$

where c^0 is the initial concentration of a complex in toluene. It was assumed that the $[M_2]/[M]$ ratio is equal to the ratio of one-half of the integrated intensity of the ESR spectral component due to the triplet-state dimers to the integrated intensity of the spectral component due to the monomers; the coefficient of one-half means that the transition of $\Delta M=1$ occurs twice within a whole-field sweep for each of the dimeric molecules, while it does so once for each of the monomeric molecules. The determination of the q value is troublesome and is responsible for the greatest error in evaluating the K value from Eq. (6). The q value was here determined by the following method.

There was a remarkable increase in the apparent intensity ratio of the ESR spectral component due to the monomers to the one due to the dimers as the c^0 value became smaller. For the monomers, accordingly, the approximate ratio of the totally-integrated spectral intensity to the height of a certain first-derivative ESR absorption line can be determined from an ESR spectrum observed in a very low concentration. Since the integrated intensity of the spectral component due to the monomers can be obtained for each of the observed ESR spectra using the above-determined ratio, the integrated intensity due to the dimers also can be determined by deducting the one due to the monomers from the totally-integrated intensity of the spectrum; the q value can then be straightforwardly evaluated from those intensity values.

The analyzed data for Cu(Etacest)$_2$, as an example, are listed in Table 2, where the q value was determined to be 0.14 ± 0.02 by using the absorption lines of H_D and H_M shown in Fig. 4. The plot of $2Q^2+qQ$ *vs.* c^0 for this complex is shown in Fig. 5. The data for

Table 2. Data on the plot of $2Q^2+qQ$ *vs.* c^0 for Cu(Etacest)$_2$ in toluene

$c^0\times10^2$ (mol/l)	H_M[a)]	H_D[a)]	$Q(=H_D/H_M)$	$2Q^2+qQ$[b)]
1.274	111.0	63.40	0.5712	0.7324
0.996	124.5	61.40	0.4932	0.5554
0.766	134.5	57.80	0.4297	0.4293
0.586	129.6	46.35	0.3576	0.3057
0.427	111.5	34.35	0.3081	0.2329
0.332	95.1	24.55	0.2581	0.1693
0.230	133.0	26.00	0.1954	0.1036
0.091	68.9	7.00	0.1016	0.0348

a) H_M and H_D (an arbitrary unit) are defined in Fig. 4.
b) The q value was assumed to be 0.14.

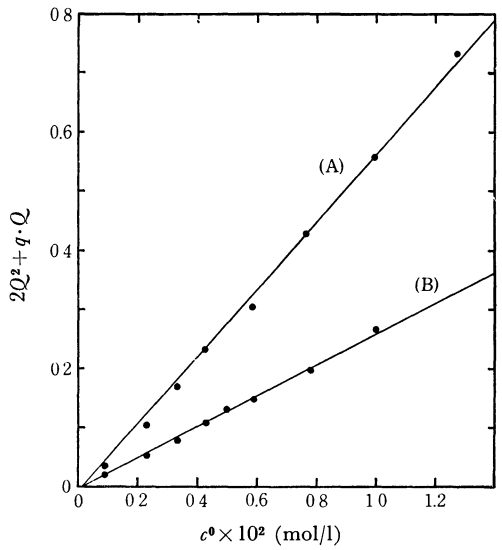

Fig. 5. The plots of $2Q^2+q\cdot Q$ vs. c^0 for (A): Cu(Etacest)$_2$ ($q=0.14$) and (B): Cu(Meacest)$_2$ ($q=0.12$).

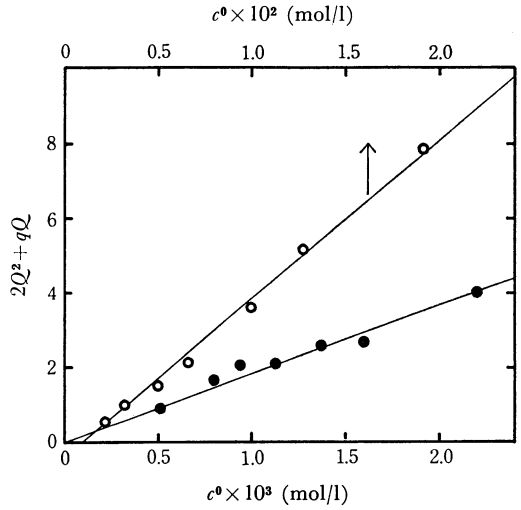

Fig. 6. The plot of $2Q^2+qQ$ *vs.* c^0.
●: $Cu(acac)_2$ ($q=0.090$)
○: $Cu(bzac)_2$ ($q=0.11$)

the other complexes are not listed here; only the plots are shown in Figs. 5 and 6. All these plots were clearly found to be linear; accordingly, the K values could be evaluated from the slopes of these linear plots. The K values thus obtained are listed in Table 3, together with the determined q values.

The fact that a plot of $2Q^2+qQ$ *vs.* c^0 gives a straight line for all the complexes in toluene indicates that both species of dimers and monomers are present in the equilibrium of Eq. (4) in the toluene solution of the complexes; the other species —for example, polymers— do not exist in the solution. The large K values determined for the first three complexes in Table 3 indicate that most molecules of the three complexes are dissolved into toluene as dimers. The linear plots above-described, furthermore, indicate that the reproducibility of this experimental method for estimating the equilibrium constants is not poor; the experimental method accompanying the solidification of the sample solutions in liquid nitrogen is applicable to various quantitative analyses, as in this case. The temperature at which the equilibrium constants are determined, however, is uncertain in this experiment, although it is undoubtedly near the freezing point of toluene (−95°C).[31,32] Such a dimer formation could not be observed in any of the various organic solvents ordinarily used other than toluene. Furthermore, bis-(dipivaloylmethanato)copper(II) and bis-(trifluoroacetylacetonato)copper(II), which are also β-diketone chelate complexes similar in various properties to $Cu(acac)_2$ and $Cu(Etacest)_2$ respectively, did not exhibit such a dimer formation in toluene; this experimental fact suggests the importance of the steric factors in the dimer formation. At any rate, the factors governing the dimer formation seem to be very complicated; a further investigation of this problem is now in progress.

Table 3. K and q[a] values

Copper(II) complex	q	$K \times 10^{-3}$
$Cu(Etacest)_2$	0.14 ±0.02	3.0 ±0.9
$Cu(Meacest)_2$	0.12 ±0.01	1.8 ±0.3
$Cu(acac)_2$	0.090±0.015	2.3 ±0.7
$Cu(bzac)_2$	0.11 ±0.01	0.35±0.05

a) See the text.

The authors wish to thank Mr. M. Chikira for many helpful discussions and suggestions during this work.

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