Triplet Dimers Observed for Several β-Diketone Chelate Complexes of Copper(II) in Toluene

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We wish to report here on the new experimental fact that triplet dimers are formed at very high concentrations in the toluene solutions of several 1:2 β-diketone chelate complexes of copper(II). In this study, the following representative β-diketone chelate complexes were employed: $Cu(Etacest)_2$, $Cu(Meacest)_2$, $Cu(acac)_2$, and $Cu(bzac)_2$, where Etacest, Meacest, acac, and bzac are the anions of ethyl acetoacetate, methyl acetoacetate acetylacetone, and benzoylacetone respectively. The X-band ESR spectrum of $Cu(Etacest)_2$ in toluene as measured at 77°K is shown as an example in Fig. 1.

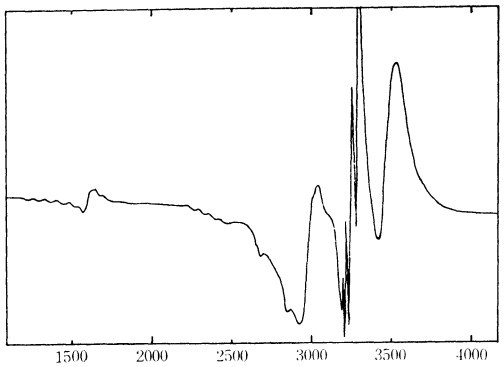

Fig. 1. The X-band ESR Spectrum of $Cu(Etacest)_2$ in toluene (c^0: 5×10^{-3} mol/l, measured at 77°K).

This spectrum clearly consists of two kinds of spectra superposed upon each other; one of them is due to monomer species (M), and the other, to triplet dimer species (D). The line shape of the latter spectrum is a typical one for magnetically-coupled Cu(II)–Cu(II) systems in the triplet state.[1-4]

It seemed that it would be very interesting to see whether or not the following type of equilibrium is established in the solution:

$$2\,M \rightleftharpoons D, \quad K=\frac{[D]}{[M]^2} \qquad (1)$$

When the observed intensity ratio between a particular ESR absorption line due to D and a particular line due to M is expressed as R, the following equation can be derived:

$$2R^2 + rR = Krc^0 \qquad (2)$$

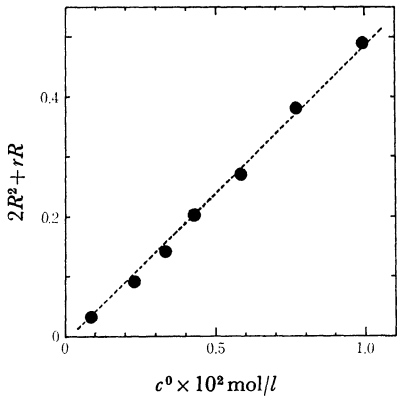

Fig. 2. A plot of $(2R^2+rR)$ against c^0 for $Cu(Etacest)_2$ in toluene

where c^0 is the initial concentration of a complex and r, the proportionality constant between R and the actual concentration ratio of D to M. The values of $(2R^2+rR)$ were plotted against c^0 for $Cu(Etacest)_2$ in toluene by putting $r=0.072$, which was the approximate value evaluated graphically from one of its ESR spectra, assuming that the actual ratio of [D] to [M] is proportional to the totally-integrated intensity ratio of the ESR absorptions of D to M. The existence of a linear relationship between them, as is shown in Fig.2, clearly indicates that the above-described equilibrium is held in the solution; accordingly, the K value could be calculated from its slope to be $(1.0\pm0.2)\times10^4$. Similarly, the K values of $Cu(Meacest)_2$, $Cu(acac)_2$, and $Cu(bzac)_2$ in toluene could be estimated to be $(6.0\pm2.0)\times10^3$, $(9.0\pm2.0)\times10^3$, and $(1.1\pm0.2)\times10^3$ respectively. The magnetic parameters determined for these systems (assuming the axial field) are listed in Table 1. The details will soon be published elsewhere, together with a discussion of these magnetic data in connection with the structures of the dimers.

Table 1. Magnetic parameters[a]

Copper(II) complex	Monomer $g_{\parallel}$	Monomer $g_{\perp}$	Monomer $A_{\parallel}\times10^3$ cm^{-1}	Monomer $A_{\perp}\times10^3$ cm^{-1}	Dimer $g_{\parallel}$	Dimer $g_{\perp}$	Dimer D cm^{-1}
$Cu(Etacest)_2$	2.29	2.05	18	2.5	2.31	2.07	0.043 ±0.004
$Cu(Meacest)_2$	2.28	2.04	18	2.5	2.30	2.07	0.040 ±0.005
$Cu(acac)_2$	2.26	2.05	19	2.5	2.29	2.06	0.018 ±0.005

a) The data of $Cu(bzac)_2$ were omitted here because of some difficulty in determining the accurate ones of its dimer species from its ESR spectra.

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