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ESR Studies of Some Copper(II) β-Diketone Chelate Complexes in Heterocyclic Basic Solvents

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Three representative copper(II) β-diketone chelate complexes, bis-(ethylacetoacetato)copper(II), bis-(salicylaldehydato)copper(II), and bis-(acetylacetonato)copper(II), have been investigated by the ESR method in order to estimate their structures in various solvents. The super-hyperfine structures due to the equal coupling of the unpaired electron with two nitrogen atoms were clearly observed for the first two complexes dissolved in pyridine or γ-picoline. The structures of these two complexes in pyridine or γ-picoline could be estimated to be as follows; a new square-planar coordination occurs through two nitrogen atoms of these basic solvent molecules and two oxygen atoms of the four originally-coordinating ligand oxygen atoms, and the other oxygen atoms are coordinated as apical ligand atoms with less strength. On the other hand, the ESR spectra of the latter complex dissolved in pyridine or γ-picoline show a significantly strong ligand field only in the axis normal to the molecular plane; this indicates that the coordination of the basic solvent molecules along the axis normal to the molecular plane occurs.

It has been reported by several authors that the reaction of copper(II) β-diketone chelate complexes with some heterocyclic bases generally produces 1 : 1- or 1 : 2-adducts.[1-3] The absorption spectral features of bis-(ethylacetoacetato)copper(II), one of the copper(II) β-diketone chelate complexes, in pyridine and piperidine are quite different from those in other ordinary solvents.[4] The ESR is a powerful and unique technique for the structural

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[1] D. P. Graddon, *Nature*, **183**, 1610 (1959); D. P. Graddon and E. C. Watton, *ibid.*, **187**, 1021 (1960).

[2] D. P. Graddon and E. C. Watton, *J. Inorg. Nucl. Chem.*, **21**, 49 (1961).

[3] Y. Muto, This Bulletin, **31**, 56 (1958).

[4] D. P. Graddon, *J. Inorg. Nucl. Chem.*, **14**, 161 (1960).

investigation of the copper(II) complexes in the following specific points: it gives much information about the strength and symmetry of the ligand field of the complexes,[5-8] and it is a method of determining decisively whether or not coordination occurs through nitrogen atoms.[9] The purpose of this paper is to estimate the structures of some copper(II) β-diketone chelate complexes in various solvents by the ESR method.

Experimental

Materials. The copper(II) β-diketone chelate complexes employed in this study are bis-(acetylacetonato)-copper(II), bis-(ethylacetoacetato)copper(II), and bis-(salicylaldehydato)copper(II); they are abbreviated as Cu(acac)$_2$, Cu(acest)$_2$, and Cu(sal)$_2$ respectively. Commercially-available Cu(acac)$_2$ was recrystallized from chloroform. The Cu(acest)$_2$ was prepared and purified according to the method in the literature.[2] The Cu(sal)$_2$ was obtained in the usual way reported in the literature by mixing an aqueous solution of cupric acetate with an ethanolic solution of salicylaldehyde, the green product being then filtered off, washed, and dried.[3,10] The adduct of [Cu(acest)$_2$(γ-picoline)$_2$] was prepared according to the method of Graddon and Watton.[2]

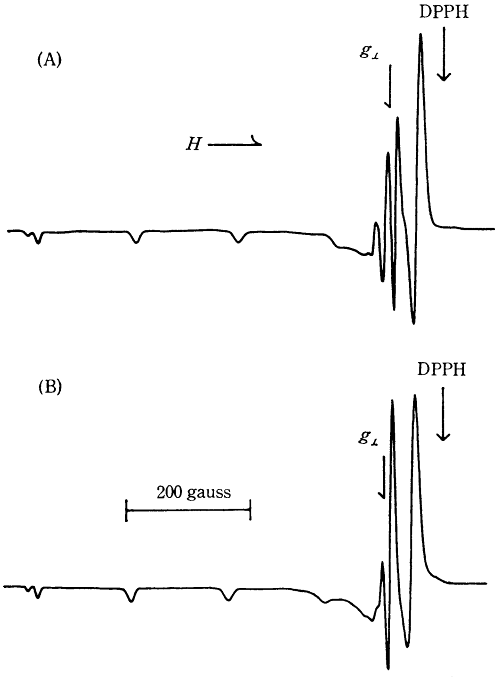

Fig. 1. The X-band ESR spectra of Cu(acac)$_2$ at 77°K.
(A) in 50% chloroform - 50% ethanol
(B) in 20% pyridine - 40% chloroform - 40% ethanol

Measurements. The ESR spectra were measured in solutions at the temperature of liquid nitrogen with a Hitachi X-band ESR spectrometer, Model MES-4001, equipped with a 100 kHz field modulation unit. Furthermore, the second derivative ESR spectra were obtained using 100 kHz-40 Hz field modulations in order to resolve the nitrogen super-hyperfine structure clearly. The field was calibrated with an NMR probe and then with a benzene solution of vanadyl acetylacetonate or with Mn(II) ions in MgO powder. Some of the ESR spectra observed are shown in Figs. 1—7, while the analyzed results are listed in Table 1. All the solvents used were mixed solvents. Almost no change in the ESR results was observed when we varied to some extent the mixing ratios of the solvents listed in Table 1.

Results and Discussion

Cu(acac)$_2$. It has been suggested, on the basis of the optical absorption and ESR spectra, that the physical and chemical properties of the β-diketone copper(II) chelate complexes in solution vary to an appreciable extent according to the kind of solvent used.[4, 11-14] The ESR data of Table 1 also clearly support the above description.

(A) in Fig. 1 shows the ESR spectrum of Cu(acac)$_2$ in 50% chloroform - 50% ethanol (volume %). This spectrum is sharp in its line width and is typical of an axial symmetry in the ligand field. (B) in Fig. 1, where the solvent is 20% pyridine - 40% chloroform - 40% ethanol, is also sharp in its absorption line width and shows the ligand field of an axial symmetry. The ESR spectrum of the complex in 10% pyridine - 90% toluene was quite similar to the (B) in Fig. 1. The absorption line shapes of these spectra indicate that there are not two or more molecular species in solution.

The ESR results of Cu(acac)$_2$ in Table 1 indicate that the addition of pyridine causes the g values to increase and the $|A_{//}|$ value to decrease. This

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[10] P. Pfeiffer, E. Breith, E. Lubbe and T. Tsumaki, *Ann.*, **503**, 84 (1933).

[11] R. L. Belford, M. Calvin and G. Belford, *J. Chem. Phys.*, **26**, 1165 (1957).

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Table 1. Magnetic parameters

Copper(II) complex	Solvent[a]	$g_{//}$	$g_{\perp}$	$\times 10^4 cm^{-1}$			
				$A_{//}$[b]	$A_{//}$ (^{65}Cu)	$A_{//}$ (^{65}Cu)	$A_{N//}$
Cu(acac)$_2$	A[c]	2.256	2.056	197			
	B	2.288	2.057		169	181	
	C*	2.304	2.060		160	173	
	E	2.297	2.062		163	175	
Cu(acest)$_2$	A	2.281	2.062		171	183	
	B	2.315	2.068		155	167	
	C	2.320	2.064	158			
	D	2.322	2.068	165			
	E	2.319	2.070	159			
	F	2.313	2.067		159	171	9.8
	G	2.318	2.070		162	174	9.7
Cu(sal)$_2$	B	2.299	2.069		153	165	
	E	2.317	2.068	162			
	F	2.312	2.070	156			
	G	2.311	2.064	168			

a) A: toluene, B: 50% chloroform-50% ethanol, C: 20% pyridine-80% toluene, C*: 10% pyridine-90% toluene, D: 20% γ-picoline-80% toluene, E: 20% pyridine-40% chloroform-40% ethanol, F: 20% pyridine-80% chloroform, G: 20% γ-picoline-80% chloroform (volume %).

b) This value was determined from the hyperfine splitting between the $I_z = \pm 1/2$ components.

c) The data were cited from a literature.[13] The almost same results were reported by Antosik *et al.*[14]

tendency of the g and $A_{//}$ values means that the ligand field of the complex on the axis normal to the molecular plane is strengthened on the addition of pyridine; the pyridine molecules coordinate to the complex as apical ligands.[8, 13, 14]

Cu(acest)$_2$ and Cu(sal)$_2$. The ESR spectra of Cu(acest)$_2$ and Cu(sal)$_2$ in 50% chloroform-50% ethanol are sharper in absorption line width than are those in other solvents, as may be seen in Figs. 2—5. An exception is the ESR spectrum of Cu(acest)$_2$ in toluene, which is shown in (B) in Fig. 2. This spectrum is different in its absorption line shape from the other spectra; it consists of a very sharp absorption-line spectrum and a broad one superposed upon each other. The former spectrum could be analyzed in the usual way; the results are listed in Table 1. The latter spectrum may be due to the triplet dimer of the complex. The observation of the broad signal at $g \doteqdot 2.0$ for the triplet dimers of some copper(II) complexes has been reported.[15] Many planar copper(II) complexes are known to have a dimer structure in the crystal,[16,17] and the dimer formation of those complexes seems to be possible in such a non-coordinating solvent as toluene. A similar spectrum was observed for Cu(acac)$_2$ in toluene. A detailed investigation of these problems is now in progress.

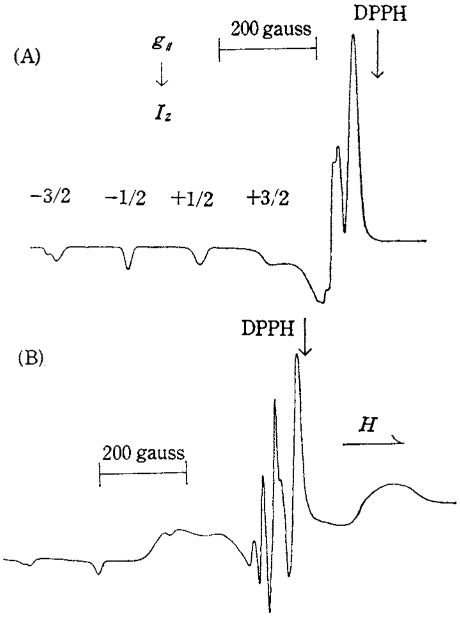

Fig. 2. The X-band ESR spectra of Cu(acest)$_2$ at 77°K.

(A) in 50% chloroform-50% ethanol

(B) in toluene

The addition of pyridine causes the absorption line width to broaden. The (A) of Fig. 3 is very broad in line width, in contrast with the (A) of

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[16] H. Koyama, Y. Saito and H. Kuroya, *J. Inst. Polytech. Osaka City Univ.*, **C4**, 43 (1953).

[17] T. N. Waters and D. Hall, *J. Chem. Soc.*, **1959**, 1203; D. Hall and T. N. Waters, *ibid.*, **1960**, 2644.

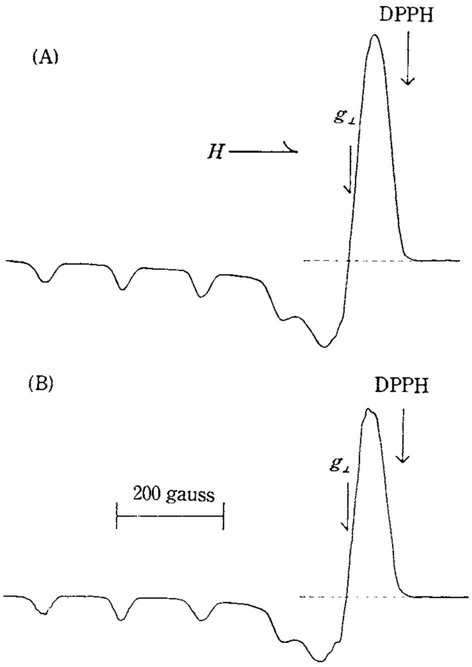

Fig. 3. The X-band ESR spectra of Cu(acest)$_2$ at 77°K.
(A) in 20% pyridine - 40% chloroform - 40% ethanol
(B) in 20% pyridine - 80% chloroform

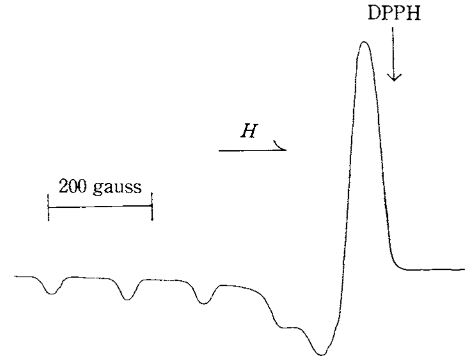

Fig. 4. The X-band ESR spectrum of Cu(acest)$_2$ in 20% γ-picoline - 80% toluene at 77°K. This spectrum was quite the same as the one of [Cu(acest)$_2$(γ-picoline)$_2$] in toluene at 77°K.

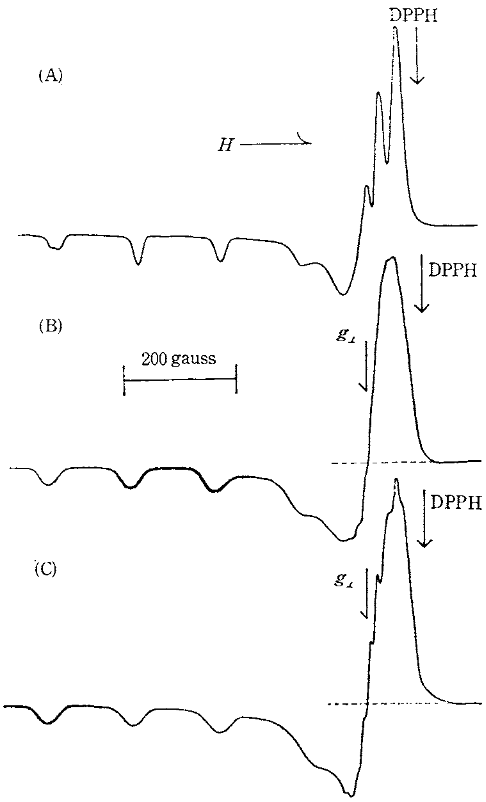

Fig. 5. The X-band ESR spectra of Cu(sal)$_2$ at 77°K.
(A) in 50% chloroform - 50% ethanol
(B) in 20% pyridine - 40% chloroform - 40% ethanol
(C) in 20% γ-picoline - 80% chloroform

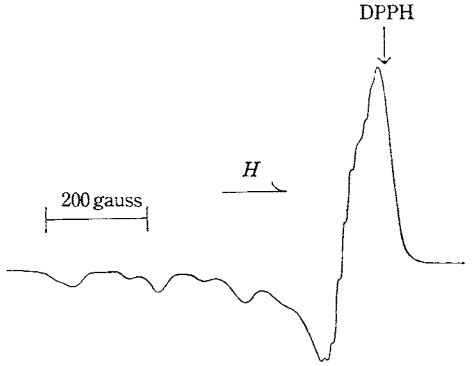

Fig. 6. The X-band ESR spectrum of Cu(acest)$_2$ in 20% piperidine - 40% chloroform - 40% ethanol at 77°K.

Fig. 2. On the other hand, piperidine, which is more basic than pyridine and γ-picoline, has a different effect on the complexes; for example, the ESR spectrum of Cu(acest)$_2$ in 20% piperidine - 40% chloroform - 40% ethanol, as is shown in Fig. 6, is due to two molecular species.

(B) in Fig. 3 shows the ESR spectrum of Cu(acest)$_2$ in 20% pyridine - 80% chloroform; this spectrum has almost the same absorption-line shape as the (A) in Fig. 3. However, the former spectrum shows more clearly than the latter one that the super-hyperfine structures appear at the most intense absorption line in the high-field part and in the hyperfine components of $I_z = -3/2$ and $-1/2$ in the low-field part. These super-hyperfine structures are considered most likely to be due to nitrogen nuclei.

The second derivative ESR spectra were measured in order to observe the super-hyperfine structures more clearly; some of them are shown in Fig. 7.

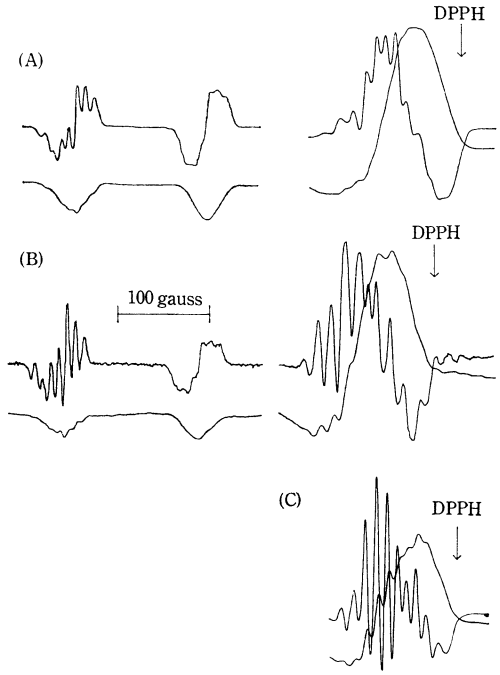

Fig. 7. The second derivative X-band ESR spectra at 77°K.
(A) Cu(acest)$_2$ in 20% pyridine-80% chloroform
(B) Cu(acest)$_2$ in 20% γ-picoline-80% chloroform
(C) Cu(sal)$_2$ in 20% γ-picoline-80% chloroform

The hyperfine and super-hyperfine structures at the most intense absorption line in the high-field part are too complex to be analyzed completely. On the other hand, the super-hyperfine structure in the hyperfine absorption lines of $I_z=-3/2$ and $-1/2$ in the low-field part were analyzed on the assumption of an equal coupling of the unpaired electron with two nitrogen atoms. The results are shown in Fig. 8, which shows a fairly good correspondence in the position and intensity of the super-hyperfine absorption line between the second derivative spectrum and its reconstruction.

The ESR spectrum of (B) in Fig. 3 shows that the ligand field of Cu(acest)$_2$ in 20% pyridine (or γ-picoline) - 80% chloroform is of an axial symmetry; the complex dissolved in the solvent has a square-planar structure. As has been described in the foregoing paragraph, the ESR spectra of Cu(acac)$_2$ in the solvents containing pyridine or γ-picoline also showed the ligand field of an axial symmetry; furthermore, it was concluded that, in the solvents, pyridine or γ-picoline molecules coordinate to the complex as apical ligands. However, no super-hyperfine structure could be observed in these spectra of Cu(acac)$_2$.

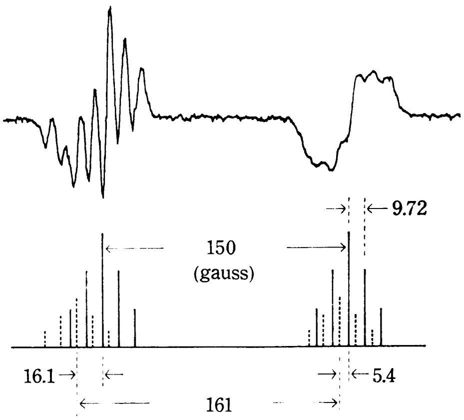

Fig. 8. The second derivative ESR spectrum (the hyperfine absorption lines of $I_z=-3/2$ and $-1/2$) of Cu(acest)$_2$ in 20% γ-picoline - 80% chloroform at 77°K and its reconstruction (solid line : ^{63}Cu dotted line : ^{65}Cu; the hyperfine intensity ratio of ^{63}Cu to ^{65}Cu of 7 : 3 was assumed).

The super-hyperfine interaction between the unpaired electron spin and the nuclear spin of the surrounding ligand atoms is mainly due to the dipole interaction and Fermi contact interaction with the spin density produced in the ligands by the covalent mixing of ligand wavefunctions into the antibonding orbitals.18-21) The super-hyperfine interaction energies listed as $A_N^{//}$ in Table 1, which were determined from the super-hyperfine structure observed in the hyperfine absorption lines of $I_z=-3/2$ and $-1/2$ in the low-field part, are comparable in magnitude to those previously reported for the square-planar copper(II) complexes containing nitrogen atoms as coordinating ligand atoms.6,9,22) When the unpaired electron orbit is on the molecular plane, the super-hyperfine interaction between the electron spin and the nuclear spin of the apical

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18) W. Marshall, "Paramagnetic Resonance," Vol. 1, ed. by W. Low, Academic Press, New York (1963), p. 347; W. Marshall and R. Stuart, *Phys. Rev.*, **123**, 2048 (1961).

19) T. P. P. Hall, W. Hayes, R. W. H. Stevenson and J. Wilkens, *J. Chem. Phys.*, **38**, 1977 (1963); **39**, 35 (1963).

20) M. Tinkham, *Proc. Roy. Soc. Ser. A* **236**, 535, 549 (1956).

21) B. R. McGarvey, "Transition Metal Chemistry," Vol. 3, ed. by R. L. Carlin, Marcel Dekker, New York (1967), p. 89; G. F. Kokoszka and G. Gordon, "Technique of Inorganic Chemistry," Vol. 7, ed. by H. B. Jonassen and A. Weissberger, Interscience Publishers, New York (1967), p. 151.

22) A. G. Gersmann and J. D. Swalen, *J. Chem. Phys.*, **36**, 3221 (1962); S. E. Harrison and J. M. Assour, "Paramagnetic Resonance," Vol. 2, ed. by W. Low, Academic Press, New York (1963), p. 855; W. Schneider and A. V. Zelewsky, *Helv. Chim. Acta*, **48**, 1529 (1965).

ligand atoms which are 2 Å or more from the metal atom, such interaction proceeding by means of direct dipole interaction or other possible mechanisms, can be estimated to be of an order of magnitude lower than the observed energies.[18-21] Therefore, it can be concluded that, in the system under discussion, two nitrogen atoms are equally introduced into the unpaired electron orbital of the complex and that a new square-planar coordination occurs through the two nitrogen atoms and the two oxygen atoms of the four originally-coordinating oxygen atoms. Needless to say, the two nitrogen atoms are those of the pyridine or γ-picoline used as the solvent.

The question next arises: what are the apical ligands in these systems. Figure 4 shows the ESR spectrum of Cu(acest)$_2$ in 20% γ-picoline - 80% toluene; this spectrum was in complete agreement with the ESR spectrum of [Cu(acest)$_2$(γ-picoline)$_2$] in toluene. This experimental fact establishes that the apical ligands are not γ-picoline molecules in either of the solutions. Furthermore, all the ESR spectra of Cu(acest)$_2$ in 20% pyridine - 80% chloroform, 20% pyridine - 40% chloroform - 40% ethanol, and 10% pyridine - 90% toluene are almost the same in line shape. This indicates that the apical ligands of the complex are same in all these solutions. From all the above discussion, it can be concluded that the apical ligand atoms are the two oxygen atoms of the four originally-coordinating oxygen atoms of Cu(acest)$_2$, whereas, as has been described above, the other oxygen atoms form a square-planar coordination. Therefore, the structure of Cu(acest)$_2$ in pyridine or γ-picoline can be visualized as is shown in Fig. 9. Such is also the case with Cu(sal)$_2$, since Cu(acest)$_2$ and Cu(sal)$_2$ are quite similar in their ESR spectral behavior.

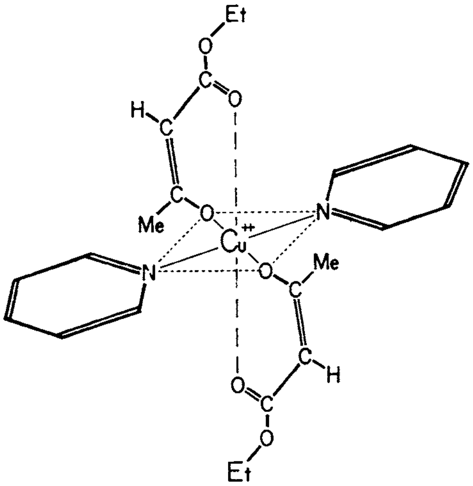

Fig. 9. The estimated structure of Cu(acest)$_2$ in pyridine.