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Single Crystal Electron Spin Resonance Spectra of Magnetically Dilute Copper(II) Ion in Some Five-coordinate Adducts of Zinc(II) β-Diketonate Complexes

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The single crystal ESR spectra of some five-coordinate adducts of copper(II)-doped zinc(II) β-diketonate complexes [Cu/Zn(acac)$_2$H$_2$O], [Cu/Zn(acac)$_2$γ-pic], [Cu/Zn(bzac)$_2$MeOH], and [Cu/Zn(bzac)$_2$py] (acac= acetylacetone anion, bzac=benzoylacetone anion, py=pyridine, γ-pic=γ-picoline, MeOH=methanol) were measured at room temperature. The principal values of the g tensor and A tensor of ^{63}Cu were calculated. The single crystal g-values of all the adducts suggested a $d_{x^2-y^2}$ ground state for the approximately square-based pyramidal structure, and were found to be consistent with crystallographic data. In the single crystals of [Cu/Zn(acac)$_2$H$_2$O] and [Cu/Zn(bzac)$_2$py], two magnetic centers were determined, this being the first time for them to have been found by ESR study.

A survey of well-known five-coordinate complexes shows the possibility of their being square pyramidal (SP) and trigonal bipyramidal (TBP). Most of them contain two bidentate ligands and one unidentate ligand. A central metal atom in the square pyramidal structure suggests two types of structure according to the coordination site of the unidentate ligand, one with a unidentate ligand in the apical position (SP-1) and the other in the basal plane (SP-2). The square-based pyramidal stereochemistry occurs much more frequently than the trigonal bipyramidal.

Bis-(*o*-hydroxyacetophenonato)γ-picoline copper(II)$^{1)}$ and bis-(acetylacetonato)quinoline copper(II)$^{2)}$ were reported to be of SP-1 structure, and bis-(acetylacetonato)4-aminopyridine copper(II)$^{3)}$ of SP-2 structure by means of X-ray crystallography. The crystal structure of monoaquobis-(acetylacetonato) zinc(II) [Zn(acac)$_2$H$_2$O] has been determined by a three-dimensional X-ray crystal-structure analysis.$^{4,5)}$ Lippert and Truter$^{4)}$ reported that zinc atom is five-coordinated with the bonds arranged in a trigonal bipyramid. On the other hand, Montgomery and Lingafelter$^{5)}$ confirmed that the structure is made up of discrete molecules, containing five-coordinate zinc(II) with an intermediate coordination configuration between tetragonal pyramidal and trigonal bipyramidal.

The powder ESR spectra of the adduct complexes of SP-1 structure, such as [Cu(acac)$_2$quinoline], [Cu(acac)$_2$γ-pic],$^{6)}$ and [Cu(bzac)$_2$py],$^{7)}$ show an axial pattern with $g_{\parallel} > g_{\perp}$ and the ground state is suggested to be $d_{x^2-y^2}$.$^{8)}$ [Cu(acac)$_2$4-aminopyridine], which forms a typical SP-2 complex, gives typical rhombic pattern (neither rhombic nor axial) of the powder ESR spectrum and the ground state is also suggested to be $d_{x^2-y^2}$. In TBP complexes, the d_{z^2} ground state is usually observed, indicating that $g_{\perp}$ is greater than $g_{\parallel}$.

In this work, the single crystals of four five-coordinate adducts of copper(II)-doped zinc(II) β-diketonate complexes were prepared and their structures were estimated by comparing the single crystal ESR spectra with crystallographic data.

Experimental

Preparation. The single crystal of the five-coordinate adducts of copper(II)-doped (1 mol%) zinc(II) β-diketonate complexes was prepared by the method of Graddon and Weeden,$^{9,10)}$ except that Zn(ClO$_4$)$_2$·6H$_2$O was used as the starting material.

Measurements. Single crystal ESR spectra were taken on a JEOL/JES-ME-3X spectrometer at room temperature. Calibration was made with a DPPH (g=2.0036). All the single crystal ESR spectra were recorded on a holder similar to that used by Hathaway and Billing,$^{11)}$ except that it was made of silica rod. As the single crystal of all the adducts decomposed easily on exposure to air, it was coated with silicone grease throughout the measurements. The crystal was rotated about three orthogonal axes and the spectra were obtained in each rotation.$^{12-15)}$

Results and Discussion

For all the complexes, well-resolved ^{63}Cu hyperfine structures were observed in the magnetically dilute single crystal ESR spectra, in which the first and last lines are partly split due to the presence of the ^{65}Cu isotope.$^{16)}$ The ESR spectra of [Cu/Zn(acac)$_2$γ-pic] and [Cu/Zn(bzac)$_2$MeOH] gave four hyperfine absorption lines. However, those of [Cu/Zn(acac)$_2$H$_2$O] and [Cu/Zn(bzac)$_2$py] gave eight lines, suggesting that there are two magnetic sites per unit cell. The single crystal ESR spectra at room temperature, shown in Figs. 1 and 2, exhibit strong Zeeman and hyperfine-

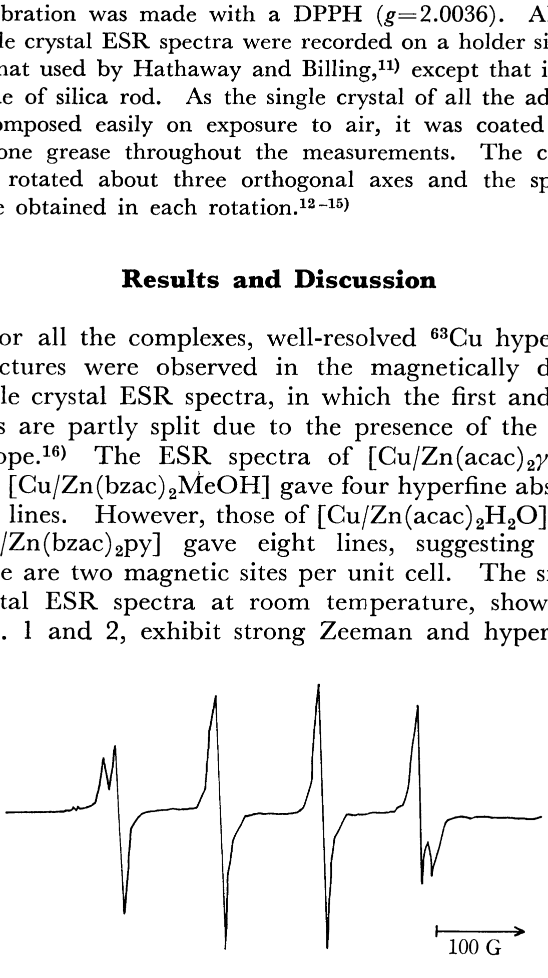

Fig. 1. ESR spectrum of [Cu(bzac)$_2$MeOH] in a [Zn(bzac)$_2$MeOH] single crystal at room temperature.

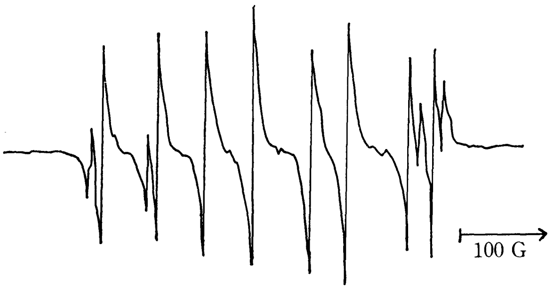

Fig. 2. ESR spectrum of [Cu(acac)$_2$H$_2$O] in a [Zn(acac)$_2$H$_2$O] single crystal at room temperature.

interaction anisotropies. Plots of the peak position as a function of the angle are shown in Figs. 3—5. The principal g- and A-values determined by the method of Schonland,[17] given in Table 1, are in agreement within experimental error with the approximate data obtained from powder ESR measurements.

a) [Cu/Zn(acac)$_2$γ-pic] and [Cu/Zn(bzac)$_2$MeOH]. These two adduct complexes yield non-axial ESR spectra (neither axial nor rhombic) with $g_1 \sim g_2 < g_3$ and $A_1 < A_2 \ll A_3$, which suggests a characteristic square pyramidal symmetry indicating $d_{x^2-y^2}$ ground state. Thus the complexes are estimated to be of SP-1 structure *i.e.*, a γ-picoline or a MeOH molecule lies at the apical position of the square pyramidal structure. The ESR spectra of [Cu/Zn(acac)$_2$γ-pic] at room temperature gave no superhyperfine interaction with a nitrogen atom of γ-picoline at the apical position of the square pyramidal structure.

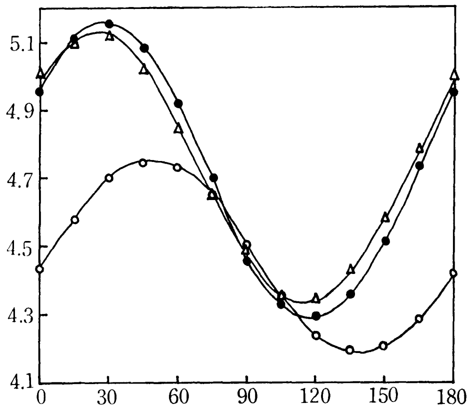

Fig. 3. Angular variations of g-value for [Cu(bzac)$_2$-MeOH] in a [Zn(bzac)$_2$MeOH] single crystal at room temperature (ESR spectra were recorded about every 15° in the three perpendicular planes. △: 1·2-plane, ○: 2·3-plane and ●: 1·3-plane).

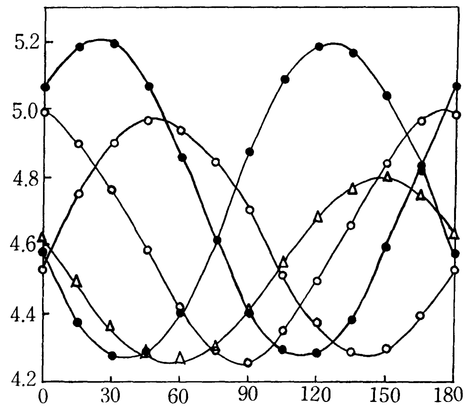

Fig. 4. Angular variations of g-value for [Cu(acac)$_2$-H$_2$O] in a [Zn(acac)$_2$H$_2$O] single crystal at room temperature (ESR spectra were recorded about every 15° in the three perpendicular planes. There are two units of this complex per unit cell. △: 1·2-plane, ○: 2·3-plane and ●: 1·3-plane).

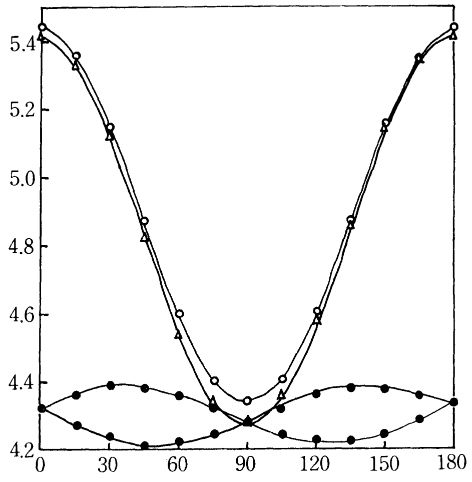

Fig. 5. Angular variations of g-value for [Cu(bzac)$_2$py] in a [Zn(bzac)$_2$py] single crystal at room temperature. (ESR spectra were recorded about every 15° in the three perpendicular planes. There are two units of this complex per unit cell. △: 1·2-plane, ○: 2·3-plane and ●: 1·3-plane).

b) [Cu/Zn(acac)$_2$H$_2$O]. Lippert and Truter[4] showed that this adduct complex forms a distorted

Table 1. Single crystal g- and A-values for five-coordinate adducts

Adduct						(G)	
		g_1	g_2	g_3	A_1	A_2	A_3
[Cu/Zn(acac)$_2$H$_2$O][a]	I	2.060	2.071	2.316	21.2	38.1	153.4
	II	2.065	2.073	2.317	20.3	37.0	152.6
[Cu/Zn(acac)$_2$γ-pic]		2.058	2.076	2.312	12.0	52.0	150.6
[Cu/Zn(bzac)$_2$MeOH]		2.045	2.094	2.312	26.8	37.2	139.9
[Cu/Zn(bzac)$_2$py][a]	I	2.055	2.094	2.330	29.4	38.9	123.8
	II	2.053	2.095	2.330	27.9	40.0	123.8

a) There are two units of this complex per unit cell.

TBP structure, whereas Montgomery and Lingafelter[5] reported it to be an intermediate configuration between SP-1 and TBP by X-ray measurements. A significant difference might be seen in the ESR spectra. Usually a $d_{x^2-y^2}$ ground state with $g_1 \sim g_2 < g_3$ is expected for SP-1 structure and a d_{z^2} ground state with $g_1 \sim g_2 > g_3$ for TBP structure. As shown in Table 1, the principal g-values for this adduct complex show $g_1 \sim g_2 < g_3$. Thus it does not seem to be of effective TBP symmetry. For [Zn(acac)$_2$H$_2$O], the distorted square-based pyramidal structure or an intermediate configuration between SP-1 and TBP, rather than the distorted TBP, could be proposed. There are two magnetic sites per unit cell, two units being symmetric in 1·2-plane but not symmetric in 1·3- and 2·3-planes, as shown in Fig. 4. The crystal is monoclinic, and the 3-axis lies approximately parallel to the crystal needle axis, *b*. This is in line with the fact that the unit cell possesses the two-fold screw axis, as was expected from X-ray analysis.[4]

c) [Cu/Zn(bzac)$_2$py]. It was found that there are two magnetic sites of [Zn(bzac)$_2$py] per unit cell from single crystal ESR spectra (Fig. 5). Measurement by the X-ray method has not yet been carried out, [Cu/Zn(bzac)$_2$py] shows principal g-values with $g_1 \sim g_2 < g_3$. This indicates the ground state to be $d_{x^2-y^2}$ which would favor the square pyramidal coordination. Thus, it seems that a pyridine molecule lies in the apical position in the square pyramidal structure. The ^{14}N superhyperfine structure of a pyridine molecule was not resolved in these ESR spectra, nor in those of [Cu/Zn(acac)$_2\gamma$-pic].

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