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ESR of Copper(II) Complexes in Magnetically Non-dilute Crystals. I. Single Crystals of Bis(L-alaninato)copper(II)

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Single-crystal ESR studies have been carried out on bis(L-alaninato)copper(II). Only one symmetric absorption peak has been obtained in any direction of the magnetic field, regardless of the fact that there are two molecules per unit cell. The principal values and the directions of the principal axes of the *g* tensor have been determined, and a correlation between those components of the *g* tensor and the crystal structure has been confirmed on the basis of the effect of the spin-exchange interaction between the dissimilar copper(II) ions. The absorption linewidths have been examined in order to estimate the spin-exchange energy.

In general, it is not easy to determine the *g* values reflecting the local copper(II)-ion environment for the magnetically non-dilute crystals or polycrystals of copper(II) complexes with polymolecular unit cells if there is an appreciable spin-exchange interaction between the dissimilar copper(II) ions.[1–5] However, the estimation of the molecular *g* values from the crystal *g* values for the crystals of chemically-complicated chelate complexes with polymolecular unit cells is occasionally desired.[6] Single crystals of bis(L-alaninato)copper(II), which have two molecules per unit cell, showed only one symmetric ESR absorption line in any direction of the magnetic field. The purpose of this paper is to present the ESR findings on undiluted single crystals in connection with the crystal structure and spin-exchange interaction between dissimilar copper(II) ions.

Experimental

Single crystals of bis(L-alaninato)copper(II) were obtained from an aqueous solution by slow evaporation. The crystals were optically identified by the use of a Stoe two-circle goniometer by measuring their interfacial angles. The crystals used in the ESR measurements were mounted on the end of a glass rod in various orientations by means of the goniometer. The ESR spectra were obtained at room temperature about each of three mutually perpendicular axes by rotation at 10 ° intervals, using a Hitachi X-band ESR spectrometer, Model-4001, equipped with a 100 kHz field modulation unit. The field was calibrated with an NMR probe and then with a benzene solution of vanadyl acetylacetonate.

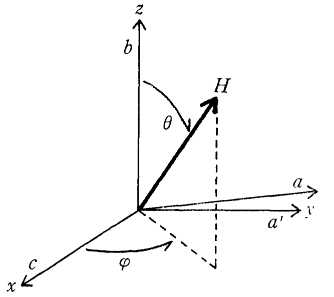

Fig. 1. A right-hand coordinate system fixed in monoclinic crystals (*a'*, *b*, and *c* are the mutually perpendicular axes).

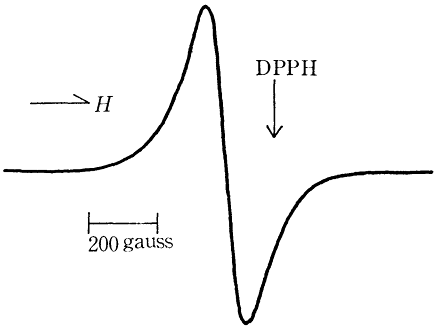

Fig. 2. The single crystal ESR spectrum of bis(L-alaninato)-copper(II) at $\theta=0°$ and $\varphi=0°$(X-band, at room temperature).

Results

Crystals of bis(L-alaninato)copper(II) are monoclinic, with a bimolecular unit with these dimensions: $a=9.24\pm0.04$, $b=5.05\pm0.02$, $c=9.59\pm0.04$ Å, and $\beta=95.2\pm0.3°$. The space group is $P2_1(C_2^2)$.[7] A right-hand system is chosen in the crystals, as is shown in Fig. 1. Only one symmetric ESR absorption peak was observed in any direction of the magnetic field. One of the observed ESR spectra is shown in Fig. 2. All the rotation data of ESR measurements are shown in Figs. 3 and 4. The rotation data concerning the *g* values were fitted by the least-squares method to expressions of the type given by Schonland,[8] diagonalization then giving the eigenvalues and vectors for the *g* tensor.

The calculated direction angles for several molecular axes are given in Table 1. The principal values for the *g* tensor are also given in the table, together with the direction angles for the principal axes. The prin-

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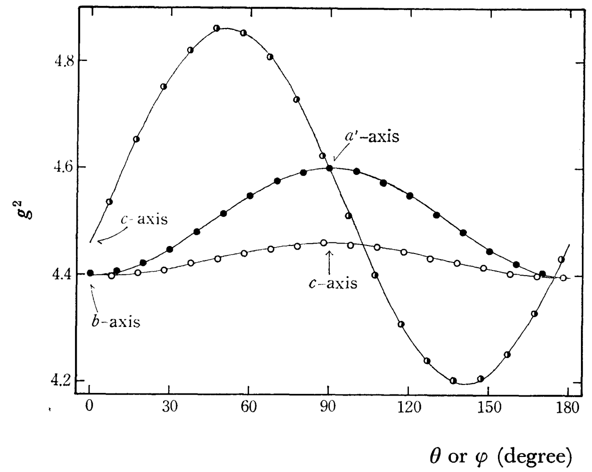

Fig. 3. The angular variance of g^2.
○: H in the bc plane, ●: H in the $a'b$ plane, ◑: H in the $a'c$ plane (the solid lines represent the calculated curves).

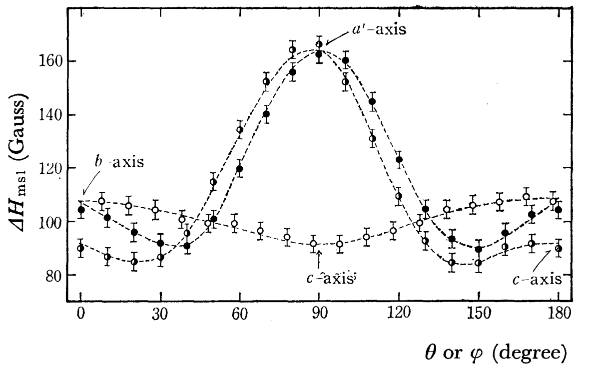

Fig. 4. The angular variance of ΔH_{msl} (the symbols are referred to in Fig. 3).

TABLE 1. THE PRINCIPAL g VALUES[a)] AND THE DIRECTION COSINES[b)] FOR THE PRINCIPAL g AXES AND SOME MOLECULAR AXES

Direction	$\cos\theta_x$[c)]	$\cos\theta_y$	$\cos\theta_z$
Cu-N(1)[d)]	0.3256	−0.6956	−0.6404
Cu-O(1)	0.8059	−0.2656	−0.5292
⊥Cu-N-O(1)	0.5414	0.6925	0.4769
Cu-N(2)[d)]	−0.3256	0.6956	−0.6404
Cu-O(2)	−0.8059	0.2656	−0.5292
⊥Cu-N-O(2)	−0.5414	−0.6925	0.4769
Internal bisector between the two ⊥ axes above	0.6159	0.7878	0
External bisector between the two ⊥ axes above	0	0	1.0
g_1=2.049	−0.7776	0.6288	0
g_2=2.096	0	0	1.0
g_3=2.203	0.6288	0.7776	0

a) Experimental errors in g factors were ±0.002. b) Experimental errors in θs were ±1.5 °. c) θ_x, θ_y, and θ_z are the angles between the indicated directions and the x, y, and z axes respectively shown in Fig. 1. d) Two molecules in an unit cell are designated by the numbers 1 and 2. N and O represent the directly coordinating atoms.

cipal g values obtained in this work agree with those determined from the powder K-band ESR spectrum by the use of the approximation of Kneubühl.[9,10]

Discussion

When there are two types of copper(II) ions with different g values, g_a and g_b respectively ($\Delta g=|g_a-g_b|$), the observed ESR line shape will depend on whether the spin-exchange energy, $2J$, is greater or smaller than $\Delta g\beta H$. If $2J>\Delta g\beta H$, only one absorption peak is to be expected, because of the unifying effect of the exchange interaction.[1—4,6] Let us now consider the case of a unit cell containing only two sets of crystallographically-non-equivalent axial molecules ($g_{//}$ and $g_{\perp}$). Let the two principal axes of the molecules be inclined at the 2γ angle. In the case of $2J>(g_{//}-g_{\perp})\beta H$, the following three principal g values ($g_1\leq g_2\leq g_3$) are given as the crystal g values:[4)]

$$g_1 = g_{\perp} \tag{1}$$

$$g_2 = \sqrt{g_{\perp}^2+(g_{//}^2-g_{\perp}^2)\sin^2\gamma} \tag{2}$$

$$g_3 = \sqrt{g_{\perp}^2+(g_{//}^2-g_{\perp}^2)\cos^2\gamma} \tag{3}$$

where the axes of g_2 and g_3 are directed to the external and internal bisectors respectively of the axes normal to two sets of crystallographically-non-equivalent molecular planes, and where the g_1 axis is perpendicular to both the g_2 and g_3 axes.

It is characteristic of the crystals of bis(L-alaninato)-copper(II) that the direction angles of the g_3 axis are in close agreement with those of the above-mentioned internal bisector, whereas those of the g_2 axis coincide with those of the external bisector, as is shown in Table 1. These experimental facts can be clearly understood from Eqs. (1)—(3). On the assumption of an axial symmetry in the molecular g values for this complex in crystals, we can determine a $g_{//}$ value which minimizes the equation of $(g_2^{\mathrm{ob}}-g_2^{\mathrm{calc}})^2+(g_3^{\mathrm{ob}}-g_3^{\mathrm{calc}})^2$, where g^{ob} represents the observed g value, and g^{calc}, the g value calculated from Eqs. (2) and (3). This $g_{//}$ value was determined to be 2.247_0 using $g_{\perp}=2.049_0$ and $\gamma=28°29'$, where the γ value is half the angle between the two above-mentioned molecular planes. Then, the calculated g values were found to be as follows:

$$g_2^{\mathrm{calc}} = 2.095_7 \text{ and } g_3^{\mathrm{calc}} = 2.203_5$$

These calculated crystal g values agree with those listed in Table 1 within the limits of experimental error. The assumption of an axial symmetry in the molecular g values for this complex in crystals contradicts a suggestion previously reported.[9)] From the point of view of chemical constitution, it had been considered that the local copper(II)-ion environment of bis(amino acidato)copper(II) complexes is rhombically distorted. However, a nearly axial symmetry in the molecular g values for this complex in crystals seems to be highly probable, since there is a satisfactory agreement between the calculated and experimentally-

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determined g values, as has been mentioned above, since various bis(amino acidato)copper(II) complexes in magnetically-diluted crystals have been reported to be of an axial symmetry in the g values11) and since it is considered that the alanine complex in crystals is not largely different from that in an aqueous solution in either the g values or the visible absorption energy; $g_{//}=2.264$, $g_{\perp}=2.056$, and $\lambda_{\max}=617$ (nm) in aqueous-methanolic solutions, whereas the above-assumed molecular g values and $\lambda_{\max}=590$ (nm) in crystals.9)

The approximate spin-exchange energy can be estimated from the observed linewidth and the calculated dipolar width using the following equations:12)

$$\Delta H = \frac{6.67(\Delta H^{\mathrm{d}})^2}{H_{\mathrm{ex}}} \tag{4}$$

$$H_{\mathrm{ex}} = \sqrt{2.83}\frac{J}{g\beta}\sqrt{S(S+1)} \tag{5}$$

where ΔH and ΔH^{d} are the observed half-width and the dipolar half-width respectively, and where H_{ex} is the exchange energy between the copper(II) ions expressed in the units of the magnetic field. It is assumed in Eqs. (4) and (5) that J is the value of the isotropic exchange interaction. ΔH^{d} can be calculated from the second moment, $<\Delta H^2>$, assuming that the line shape is of Gaussian form:

$$\Delta H^{\mathrm{d}} = 2.35\sqrt{\langle \Delta H^2 \rangle} = 2.35\left[\frac{3}{4}\mu^2\sum_{i,j}\frac{(3\cos\theta_{ij}-1)^2}{{r_{ij}}^6}\right]^{1/2} \tag{6}$$

where μ is the magnetic moment, where r_{ij} is the distance between the copper ions i and j, and where θ_{ij} is the angle between r_{ij} and the static magnetic field. Instead of ΔH, the separation between the points of the maximum and minimum slopes, ΔH_{msl}, was used for all the calculations, with an appropriate correction. The results are summarized in Table 2. The estimated J values in the table slightly differ with different directions of H. The reason for this may be that Eqs. (4) and (5) are approximate equations for the present case, since they are valid only when the g tensor is isotropic,1,12) and that the effect of hyperfine coupling on the linewidth is neglected in these equations.12) It is expected that the actual J value in the crystals of bis(L-alaninato)copper(II) is slightly larger than those listed in Table 2 because of the broadening effect of the hyperfine structure, and that this effect becomes more profound with g in the indicated directions of H in the table. In conclusion, J is of the order of 0.5 cm^{-1} for this complex in crystals.

TABLE 2. ESTIMATION OF THE J VALUE

Direction of H	g	ΔH_{msl} (gauss)	$\Delta H^{\mathrm{d}}_{\mathrm{msl}}$ (gauss)	J (cm^{-1})
$a' // H$	2.143	164	344	0.33
$b // H$	2.096	108	364	0.55
$c // H$	2.110	92	293	0.42

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