ESR of Copper(II) Complexes in Magnetically Non-dilute Crystals. II. Polycrystals of Various Bis(amino acidato)copper(II) Complexes

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(Received February 24, 1973)

The molecular *g* values of several bis(amino acidato)copper(II) complexes in crystals, whose crystal structures with two molecules per unit cell are known, have been estimated from the crystal *g* values by considering the effect of the spin-exchange interaction between the dissimilar copper(II) ions. All the crystal *g* values have been determined here from the powder K-band ESR spectra. Many other complexes with unknown crystal structures have also been dealt with in a similar way. The results have indicated that most of the complexes probably have a tetragonal or nearly tetragonal copper(II) ion environment in crystals, and a tendency for the estimated $g_{//}$ value to decrease with an increase in the energy of the visible absorption peak in crystals have been noted. A discussion about the correlation between an axial molecular *g* tensor and the two copper-ligand bond lengths of Cu–O and Cu–N has been given.

In previous papers,[1,2] it has been suggested that the copper(II) ion environment in most bis(amino acidato)-copper(II) complexes in crystals may be rhombically distorted because of two different kinds of atoms (O and N) directly coordinating to the metal ion. This has been supported by the fact that almost all the powder ESR spectra of the complexes show three different principal *g* values.[1] On the other hand, however, it has been reported that some bis(amino acidato)copper(II) complexes in magnetically diluted crystals and almost all the complexes in frozen aqueous methanolic solutions are of an axial symmetry in their *g* values.[1–3] Recently, an ESR study of bis(L-alaninato)copper(II) in undiluted single crystals has also revealed that a tetragonal molecular *g* tensor can be estimated from the observed rhombic *g* tensor of the crystal bulk by considering the crystal structure and the effect of the spin-exchange interaction between the dissimilar copper(II) ions.[4] Therefore, it seems necessary at present to reinterpret the powder ESR results previously reported after giving thought to the spin-exchange interaction in magnetically non-dilute crystals.

The purpose of this paper is to estimate the molecular *g* values from the crystal values for various bis(amino acidato)copper(II) complexes in crystals in view of the above-mentioned spin-exchange effect, and to discuss the correlation among the estimated molecular *g* values, the crystal structures, and the ligand-field properties.

Experimental

The K-band ESR spectra were measured in a polycrystalline state at room temperature with a Hitachi ESR spectrometer, Model-4001. The principal crystal *g* values (the principal *g* values of the crystal bulk) were determined from the powder ESR spectra by the use of the approximation of Kneubühl.[5]

The copper(II) complexes of amino acids employed in the present ESR measurements were as follows: bis(α-amino-iso-butyrato)copper(II), bis(L-threoninato)copper(II) monohydrate, bis(*N*,*N*-dimethylglycinato)copper(II) trihydrate, and bis(L-hydroxyprolinato)copper(II) monohydrate (abbreviated as [Cu(Aib)$_2$], [Cu(L-Thr)$_2$]·H$_2$O, [Cu(Dmg)$_2$]·3H$_2$O, and [Cu(L-Hypro)$_2$]·H$_2$O respectively). They were all prepared according to the usual method,[6] using commercial G.R.-grade α-amino acids, were recrystallized from water, and were identified by elemental analysis. The visible absorption spectra for these complexes in a polycrystalline state were measured using the opal-glass method previously described.[1] Only the absorption peak positions (λ_{max}) will

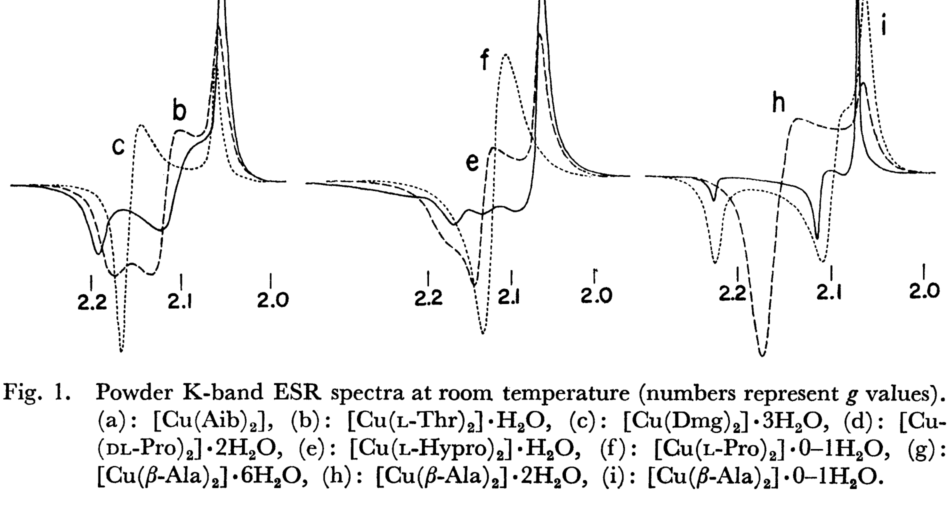

Fig. 1. Powder K-band ESR spectra at room temperature (numbers represent *g* values). (a): [Cu(Aib)$_2$], (b): [Cu(L-Thr)$_2$]·H$_2$O, (c): [Cu(Dmg)$_2$]·3H$_2$O, (d): [Cu(DL-Pro)$_2$]·2H$_2$O, (e): [Cu(L-Hypro)$_2$]·H$_2$O, (f): [Cu(L-Pro)$_2$]·0–1H$_2$O, (g): [Cu(β-Ala)$_2$]·6H$_2$O, (h): [Cu(β-Ala)$_2$]·2H$_2$O, (i): [Cu(β-Ala)$_2$]·0–1H$_2$O.

be reported here, with an error of ±4 nm.

Bis(β-alaninato)copper(II) hexahydrate is known to effloresce in air at room temperature. After the powdered hexahydrate complex had been allowed to stand in air at room temperature for several hours (resulting in Compound (I)), its powder K-band spectrum was measured; then, the K-band spectrum also was measured for the complex obtained by heating Compound (I) *in vacuo* at 120 °C for two hours (resulting in Compound (II)).[7] Recently, Misumi *et al.* determined the hydration degree for each of the complexes obtained in the course of the dehydration of the hexahydrate complex; they also measured the powder X-band ESR spectra of the complexes.[8] By a comparison between the ESR spectra reported by them and those shown in this paper, Compounds (I) and (II) can be regarded as $[Cu(\beta\text{-Ala})_2]\cdot 2H_2O$ and $[Cu(\beta\text{-Ala})_2]\cdot 0\text{—}1H_2O$ respectively. $[Cu(\text{L-Pro})_2]\cdot 2H_2O$ was also dehydrated *in vacuo* at 120 °C for two hours (the degree of hydration for this complex, which is abbreviated as $[Cu(\text{L-Pro})_2]\cdot 0\text{—}1H_2O$, was not checked here). The powder ESR spectrum of $[Cu(\text{DL-Pro})_2]\cdot 2H_2O$ was again measured after repeated recrystallizations from water. All the powder ESR spectra measured in this work are shown in Fig. 1. $[Cu(\beta\text{-Ala})_2]\cdot 6H_2O$, $[Cu(\text{L-Pro})_2]\cdot 2H_2O$, and $[Cu(\text{DL-Pro})_2]\cdot 2H_2O$ are the complexes which had been prepared in previous works.[1,2] The abbreviations for the other bis(amino acidato)copper(II) complexes cited in this paper are the same as have been reported previously.[1,2]

Results and Discussion

Estimation of Molecular g Values. We will now consider the case of a unit cell containing only two sets of crystallographically non-equivalent axial molecules, whose principal g values are represented by $g_{//}$ and $g_\perp$ ($g_{//}>g_\perp$). Let the two principal axes of the molecules be inclined at an angle of 2γ. In the condition of $2J>(g_{//}-g_\perp)\beta H$, the three principal crystal g values ($g_1\leq g_2\leq g_3$ for $0°\leq\gamma\leq 45°$) are expressed as follows:[9]

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

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

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

where the g_3 and g_2 axes are directed to the internal and external bisectors respectively of the axes normal to the two non-equivalent molecular planes, and where the g_1 axis is perpendicular to both the g_2 axis and the g_3 axis. The powder ESR line shape of a reverse-type ($g_1<g_2=g_3$) is observed for any one of the complexes, with $\gamma=45°$ in crystals. Strictly speaking, Eqs. (1)—(3) are incorrect for the above-described system, since g_2 and g_3 must be expressed as $g_\perp+(g_{//}-g_\perp)\sin^2\gamma$ and $g_\perp+(g_{//}-g_\perp)\cos^2\gamma$ respectively, because of the following form of the Zeeman term in the effective spin Hamiltonian under such a spin-exchange field: $(\beta/2)(\boldsymbol{S}^1+\boldsymbol{S}^2)(\boldsymbol{g}_a+\boldsymbol{g}_b)\boldsymbol{H}$, where the two paramagnetic species are denoted by a and b and where the electrons are denoted by 1 and 2.[10] However, as the anisotropy in the molecular g tensor for copper(II) complexes is not so large, Eqs. (1)—(3) can be used in numerical calculations without any serious errors in this work; so can Eq. (4), which will be discussed later.

Equations (1)—(3) were successfully applicable to the case of $[Cu(\text{L-Ala})_2]$ in crystals. The results alone are presented in Table 1. The $g_{//}$ and $g_\perp$ values of $[Cu(Pen)_2]$ in crystals were determined from Eqs. (1)—(3), using the γ value determined by X-ray analysis so as to minimize the equation of $(g_2^{ob}-g_2^{calc})^2+(g_3^{ob}-g_3^{calc})^2$.[11] The results are listed in Table 1. The values of g_2^{calc} and g_3^{calc} for this complex are in agreement with the experimentally-determined values of g_2^{ob} and g_3^{ob} respectively within the limits of experimental error. $[Cu(\text{DL-}\alpha\text{-NH}_2\text{but})_2]$ and $[Cu(\text{DL-Met})_2]$, whose γ values are not known,[12,13] show powder ESR line shapes similar to those of $[Cu(\text{L-Ala})_2]$ and $[Cu(Pen)_2]$; the values of $g_{//}$, $g_\perp$, and γ for the former two complexes were tentatively calculated from Eqs. (1)—(3) using the observed crystal g values. The γ values thus calculated were close to those of the latter two complexes, as is shown in Table 1. This result can be well understood from the point of view of crystal structure; all these four complexes are monoclinic, with a space group of the $P2_1$ type, and all may be expected to have almost the same inter-molecular interaction in crystals. The molecular g values thus estimated, therefore, may be substantially correct.

The powder ESR spectrum of $[Cu(\text{L-Ser})_2]$ has a typical reverse-type line shape ($g_1^{ob}<g_2^{ob}\fallingdotseq g_3^{ob}$), as has been shown previously.[2] The γ value of this complex was determined by X-ray analysis to be close to 45°.[14] Its observed crystal g values, therefore, can be qualitatively explained from Eqs. (1)—(3) using such a large γ value as is listed in Table 1. The powder ESR line shape of $[Cu(\text{DL-Pro})_2]\cdot 2H_2O$ is also of a reverse-type, as is shown in Fig. 1. Its reverse-type line shape alone can be qualitatively explained in terms of the fact that its γ value is close to 45°. Some other complicated factors, however, must be considered in order to explain the complexity of its line shape.

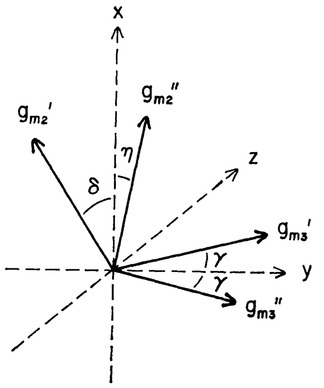

Fig. 2. A coordinate system for two non-axial molecules per unit cell.

The possibility, however, can not be denied that certain complexes might have non-axial molecular tensors. The equations corresponding to Eqs. (1)—(3) are complicated for this non-axial case;[15,16] besides γ, they require two new angles (δ and η), which will be defined below. The three principal molecular g values are denoted by g_{m1}, g_{m2}, and g_{m3} in order of increasing magnitude. The y and z axes are defined so as to bisect the angle between the two non-equivalent molecular axes (the two g_{m3} axes) internally and ex-

TABLE 1. CRYSTAL g VALUES, MOLECULAR g VALUES, AND CRYSTAL STRUCTURES

No.	Copper(II) complex	Crystal g values		Molecular g values $g_\perp$ $g_{//}$	λ_{max} (nm)	Crystal structures			Ref.
						(degree) γ	Bond lengths (Å) (the mean)		
		Obsd[c)]	Calcd				Cu–N	Cu–O	
1	[Cu(L-Ala)$_2$][b)]	2.049	2.049	2.049	590	28.5	2.015	1.965	17
		2.096	2.096	2.247					
		2.203	2.204						
2	[Cu(Pen)$_2$]	2.053	2.053	2.053	535	29.8	1.98	1.91	11
		1.089	2.089	2.195					
		2.160	2.161						
3	[Cu(β-Ala)$_2$]•6H$_2$O	2.068	2.068	2.068	635	29.8	2.04	2.01	18
		2.109	2.119	2.266					
		2.223	2.219						
4	[Cu(L-Ser)$_2$][d)]	2.056	2.056	2.056	603	41.8	1.982	1.961	14
		2.157	2.146	2.254					
		2.157	2.168						
5	[Cu(DL-Pro)$_2$]•2H$_2$O[e)]	(reverse-type g values)		(rhombic g values)	605	40.2	1.99	2.03	19
6	[Cu(DL-α-NH$_2$but)$_2$][f)]	2.052	2.052	(2.052)	585	(28.5)			12
		2.098	2.098	(2.247)					
		2.204	2.204						
7	[Cu(DL-Met)$_2$][f)]	2.053	2.053	(2.053)	580	(30.1)	1.983	1.951	13
		2.100	2.100	(2.234)					
		2.190	2.190						
8	[Cu(β-NH$_2$but)$_2$]•2H$_2$O	2.044			655	0	1.992	2.004	20
		2.090							
		2.280							

a) All the complexes have two molecules per unit cell except [Cu(β-NHbut)$_2$]•2H$_2$O, which has one molecule per unit cell. b) See Ref. 4. c) Experimental errors in g factors were ± 0.003. d) Larger errors may be expected in the two large crystal g values, because the powder ESR line shape of this complex deviates slightly from a complete reverse-type. e) See the text. f) The assumed values are expressed in parentheses (see the text).

ternally respectively, while the x axis is defined as perpendicular to the plane containing the two molecular axes (Fig. 2). In this coordinate system, δ and η specify the inclination of the two sets of g_{m2} axes to the x-axis. In general, the relation of $\delta=180°-\eta$ holds, since molecules are often related by screw-diad axes, as in the case of the complexes in Table 1. Accordingly, the elements of the g^2 matrix in this coordinate system may be expressed as follows:

$$
\begin{aligned}
g^2_{xx} &= g^2_{m1} + (g^2_{m2}-g^2_{m1}) \cos^2 \delta \\
g^2_{yy} &= g^2_{m2} \cos^2 \gamma + g^2_{m2} \sin^2 \gamma - (g^2_{m2}-g^2_{m1}) \sin^2 \gamma \cos^2 \delta \\
g^2_{zz} &= g^2_{m3} \sin^2 \gamma + g^2_{m2} \cos^2 \gamma - (g^2_{m2}-g^2_{m1}) \cos^2 \gamma \cos^2 \delta \\
g^2_{xz} &= (1/2)(g^2_{m2}-g^2_{m1}) \cos \gamma \sin 2\delta \qquad (4)
\end{aligned}
$$

Here, $g^2{}_{yz}$ and $g^2{}_{xy}$ are reduced to zero by the relation of $\delta=180°-\eta$. The observed principal crystal g values (g_a, g_b, and g_c) are obtained by diagonalizing the above matrix; in this case, the following convenient equations can be derived:

$$
\begin{aligned}
g_a{}^2 &= g^2_{yy} \\
g_a{}^2 + g_c{}^2 &= g^2_{xx} + g^2_{zz} \\
g_a{}^2 \cdot g_c{}^2 &= g^2_{xx} \cdot g^2_{zz} - (g^2_{xz})^2 \qquad (5)
\end{aligned}
$$

There have been almost no data concerning the δ except for a few copper(II) complexes. The crystal g values (g_a, g_b, and g_c) for each of the properly-assumed

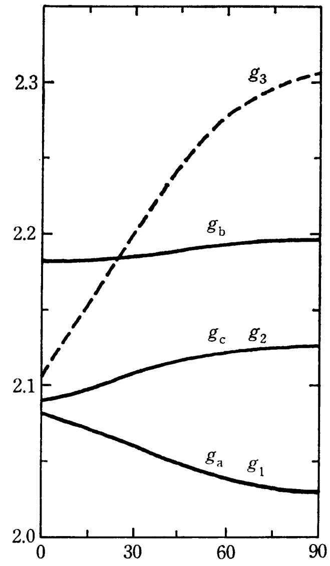

Fig. 3. The three principal crystal g values (g_a, g_b, and g_c; they are expressed as solid lines) derived from Eqs. (4) and (5) using $g_{m1}=2.030$, $g_{m2}=2.090$, $g_{m3}=2.230$, and $\gamma=30°$. The dashed line represents the g_3 value derived from Eq. (3) on the assumption of $g_1=g_a$ and $g_2=g_c$ in Eqs. (1) and (2).

sets of the g_{m1}, g_{m2}, g_{m3}, γ, and δ values were calculated from Eqs. (4) and (5). Then, it was examined whether or not the g_1, g_2, and g_3 values derived from Eqs. (1)—(3) using a proper set of the $g_{//}$ and $g_\perp$ values and the same γ value could be fitted to the g_a, g_b, and g_c values calculated above. Some of the results are shown in Fig. 3. This figure indicates that the g_a, g_b, and g_c values calculated for $\gamma=30°$, $g_{m1}=2.030$, $g_{m2}=2.090$, and $g_{m3}=2.230$ are not equal to the g_1, g_3, and g_2 values respectively except for the case of $\delta=25°$ (an intersection of solid and dashed lines in this figure). Furthermore, it became apparent that such an intersection varies over a wide range of δ according to the g_{m1}, g_{m2}, g_{m3}, and γ values. Since it is very rare for an actual case to correspond to the case of such an intersection, it is highly probable that the g tensors of copper(II) complexes in crystals are of an axial or nearly axial symmetry, if their crystal g values, as calculated from Eqs. (1)—(3) using proper sets of the $g_{//}$ and $g_\perp$ values, can be fitted to the observed values within the limits of experimental error. Accordingly, there is very little doubt that [Cu(Pen)$_2$] in crystals has an axial g tensor as well as [Cu(L-Ala)$_2$], as has been mentioned above. On the other hand, it was found that, when γ is close to 45°, g_b becomes close to g_c for any value of δ; accordingly, it is difficult to judge whether the observed crystal g values of a reverse-type ($g_1^{ob}<g_2^{ob}=g_3^{ob}$) correspond to the g_a, g_b, and g_c values or to the g_1, g_2, and g_3 ones. In this case, another method for judging whether or not the $g_{//}$ and $g_\perp$ values tentatively estimated from the observed g values are correct is required.

Support for the view that all the $g_{//}$ and $g_\perp$ values listed in Table 1 are close to the true molecular g values comes also from the fact that the tendency for the $g_{//}$ value to decrease regularly with an increase in the energy of λ_{max}, as is shown by full circles in Fig. 4, is consistent with the same tendency previously recognized for a great numer of copper(II) complexes in frozen solutions.[21)]

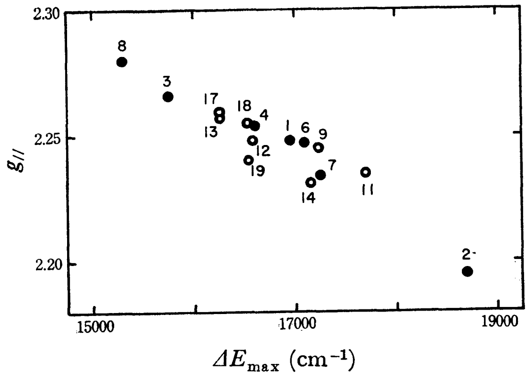

Fig. 4. A plot of $g_{//}$ against ΔE_{max} (numbers correspond to the complexes in Tables 1 and 2; open circles correspond to the complexes with unknown crystal structures listed in Table 2).

The values of $g_{//}$, $g_\perp$, and γ for a number of bis(amino acidato)copper(II) complexes whose crystal structures are not known were determined from the observed crystal g values using Eqs. (1)—(3), on the assumption that all these complexes have axial g tensors in crystals; the results are listed in Table 2. All the reverse-type crystal g values observed for several complexes led to the result of $\gamma=45°$. The fact that all the determined γ values of the anhydrous complexes in Table 2 are close to 30° is consistent with the fact noted for the anhydrous complexes in Table 1. There is also a slight tendency for the $g_{//}$ value thus estimated to decrease with an increase in the energy of λ_{max} in crystals, as is shown by open circles in Fig. 4. The molecular g values listed in Table 2 may, therefore, be substantially correct.

The ESR spectra of the hydrated copper(II) complexes generally show drastic changes in line shape when the complexes are dehydrated to a varying extent, as is shown by some examples in Fig. 1. It seems unnatural, however, that the molecular g values of the hydrates are markedly altered only by such a dehydration. For instance, [Cu(β-Ala)$_2$]·6H$_2$O and [Cu(DL-Ala)$_2$]·H$_2$O showed almost no marked changes in the

Table 2. Crystal and molecular g values for the complexes with unknown crystal structures

No.	Copper(II) complex	Observed values				Assumed values b)		
		Crystal g values a)			λ_{max} (nm)	Molecular g values		γ (degree)
		g_1^{ob}	g_2^{ob}	g_3^{ob}		$g_\perp$	$g_{//}$	
9	[Cu(DL-Ala)$_2$]·H$_2$O	2.053	2.122	2.180	580	2.053	2.245	36.2
10	[Cu(DL-Ala)$_2$]	2.054	2.100	2.202		2.054	2.245	28.8
11	[Cu(Aib)$_2$]	2.051	2.102	2.187	565 c)	2.051	2.235	31.2
12	[Cu(DL-Val)$_2$]	2.056	2.105	2.202	603	2.056	2.248	29.8
13	[Cu(DL-Ser)$_2$]	2.058	2.111	2.208	615	2.058	2.257	30.4
14	[Cu(L-Thr)$_2$]·H$_2$O	2.058	2.116	2.176	583	2.058	2.231	34.8
15	[Cu(β-Ala)$_2$]·2H$_2$O	2.062	2.171	2.171		2.062	2.275	45.0
16	[Cu(β-Ala)$_2$]·0—1H$_2$O	2.060	2.095	2.224		2.060	2.256	24.5
17	[Cu(Dmg)$_2$]·3H$_2$O	2.058	2.161	2.161	615	2.058	2.259	45.0
18	[Cu(L-Pro)$_2$]·2H$_2$O	2.056	2.158	2.158	605	2.056	2.255	45.0
19	[Cu(L-Hypro)$_2$]·H$_2$O	2.061	2.129	2.175	605	2.061	2.240	37.5

a) Experimental errors in g factors are ±0.003. b) The observed crystal g values can be calculated from Eqs. (1)—(3) using the assumed γ and molecular g values. c) Since the absorption spectrum is composed of two broad bands (about 525 and 610 nm), the mean was adopted for convenience.

estimated molecular g values upon dehydration, as is shown in Table 2, nor were there any remarkable accompanying color changes. It is of interest that the reverse-type powder ESR line shape of $[\mathrm{Cu(L\text{-}Pro)_2}]\cdot 2\mathrm{H_2O}$ changed into a nearly symmetric one when this complex was dehydrated to a certain degree, as is shown in Fig. 1(f). It is more likely that the molecular g values for this complex also are not markedly altered upon dehydration, and that the symmetric powder ESR line shape is due to a special type of molecular packing in crystals; for instance, such a symmetrical line is observed if the four axial molecules are arranged with their molecular axes pointing towards the corners of a tetrahedron.[16]

Symmetry of the Ligand Field. Recently, many ESR studies have indicated that the molecular g tensors of the copper(II) complexes with different coordinating atoms in the molecular plane are of an axial or nearly axial symmetry. Almost all of the mixed-ligand complexes of copper(II) in solution so far examined have shown ESR line shapes of an axial type.[22] It is a well-known fact that the ability of some familiar ligand atoms to coordinate to the copper atom is in the order of S>N>O. The copper(II) chelates of monothio-β-diketones also have nearly axial g and A tensors in various magnetically-diluted states.[23] These facts suggest that, especially in solution, most copper(II) complexes generally tend to be of an axial or nearly axial symmetry in the g and A tensors, even if their coordinating atoms are different in kind.

Most of the complexes listed in Table 1 also have axial or nearly axial molecular g tensors in crystals; it is worthy of special attention that all the Cu–O bonds of these complexes are shorter by 0.03—0.07 Å than the Cu–N ones. On the other hand, the Cu–O bonds of $[\mathrm{Cu(\beta\text{-}NH_2but)_2}]\cdot 2\mathrm{H_2O}$ are slightly longer than the Cu–N ones, and its molecular g tensor is clearly rhombic. $[\mathrm{Cu(L\text{-}Ser)_2}]$ is known to adopt a *cis*-configuration. The Cu–O bonds of this complex also are shorter by 0.020 Å (the mean) than the Cu–N ones. In general, the *cis*-complexes of copper(II), whose four coordinating atoms take a planar conformation of C_{2v} symmetry, as is approximately the case with $[\mathrm{Cu(L\text{-}Ser)_2}]$, tend to have axial or nearly axial g tensors, since even the possible lateral distortions (a distortion type of $Y^1_{1,3}$ in the crystal-field theory) in such *cis*-complexes do not destroy the axial symmetry in the molecular g tensor.[24]

Let us now consider the above-mentioned relation between the coordinate bond lengths and the axial g tensor. An axial molecular g tensor roughly means that $2-2\lambda_0(\alpha^2\mu^2/\Delta E_{xz})=2-2\lambda_0(\alpha^2\nu^2/\Delta E_{yz})$, where λ_0 represents the spin-orbit coupling constant for the free copper(II) ions, where $\Delta E_{xz}=E_{x^2-y^2}-E_{xz}$ and $\Delta E_{yz}=E_{x^2-y^2}-E_{yz}$, and where α, μ, and ν are the coefficients of the metal $3d$ atomic orbitals in the following antibonding molecular orbitals: $\phi_\alpha=\alpha d_{x^2-y^2}-\alpha'\phi_\alpha{}^{\mathrm{L}}$, $\phi_\mu=\mu d_{xz}-\mu'\phi_\mu{}^{\mathrm{L}}$, and $\phi_\nu=\nu d_{yz}-\nu'\phi_\nu{}^{\mathrm{L}}$ (ϕ^{L}s express the proper ligand orbitals).[25] One of the conditions which satisfy the equation of $(\alpha^2\mu^2/\Delta E_{xz})=(\alpha^2\nu^2/\Delta E_{yz})$ for the *trans*-complexes is as follows: the energy levels of $\phi_\mu{}^{\mathrm{L}}$ and $\phi_\nu{}^{\mathrm{L}}$ are close to each other, and, in addition, the square values of the overlap integral in the ϕ_μ and ϕ_ν molecular orbitals are almost equal.[26] Although the oxygen $2s$ and $2p$ atomic orbitals generally lie at lower energy levels than the respective nitrogen ones, it can reasonably be considered that the oxygen energy levels in the complexes of amino acids are raised to a great extent because of the oxygen atoms coordinated to the metal atom as a part of negatively-charged carboxyl anions.[27]

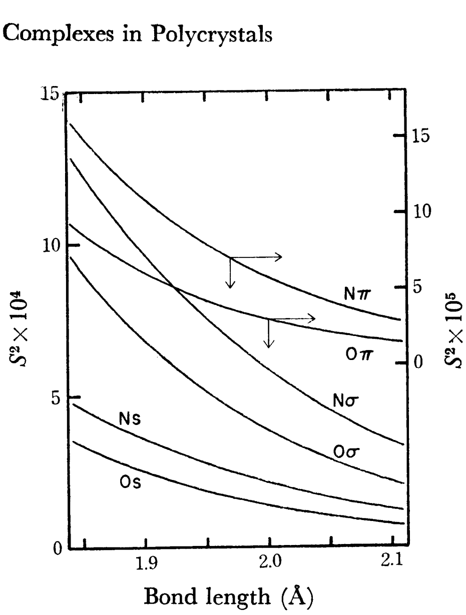

Fig. 5. Variations of the squares of overlap integrals with bond length (Ns, Nσ, and Nπ represent $[S(3d\sigma-2s)]^2$, $[S(3d\sigma-2p\sigma)]^2$, and $[S(3\pi d-2p\pi)]^2$ respectively for the Cu–N bond, and Os, Oσ, and Oπ do so for the Cu–O bond).

The square values of the overlap integral, S, for the Cu–O and Cu–N bonds were calculated from the Slater atomic orbitals by the use of the single-ζ exponent values given by Clementi and Raimondi,[28] assuming that the copper and nitrogen atoms are electrically neutral and that the oxygen atom is negatively charged by a half unit; for the oxygen $2s$ and $2p$ orbitals, $\zeta=\zeta_n-0.35\ (q/n)$, where ζ_n represents the ζ value of electrically-neutral oxygen atoms, where 0.35 means the shielding constant, and where q is the charge, and n, the principal quantum number ($q=1/2$, $n=2$).[29] The numerical calculations were carried out on the NEAC-2200 Model-700 (TSS) computer at Tohoku University. The results are shown in Fig. 5. This figure indicates that the square values of $S(3d\sigma\text{-}2s)$, $S(3d\sigma\text{-}2p\sigma)$, and $S(3d\pi\text{-}2p\pi)$ for the Cu–O bonds become equal to those for the respective Cu–N bonds when the Cu–O bonds are shorter than the Cu–N ones by about 0.07 Å for the former two S's and by about 0.09 Å for the latter. This result can qualitatively explain the above-mentioned fact that it is required for an axial g tensor that the Cu–O bonds are shorter by about 0.05 Å than the Cu–N ones. This result is also almost consistent with the concept of covalent bond radii; the covalent radius of N is larger by 0.04 Å than that of O.[30]

It may be concluded from all the experimental results listed in Tables 1 and 2 that almost all bis(amino acidato)copper(II) complexes in crystals, except for a small number, are of an axial or nearly axial symmetry in the copper(II) ion environment.

The author is grateful to Professor Taro Isobe for his encouragement throughout this work.

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