EPR STUDY OF GLYCINE-COPPER COMPLEXES IN AQUEOUS SOLUTION

By A. M. Dezor

Institute of Molecular Physics of the Polish Academy of Sciences, Poznań*

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Results of investigation of glycine-copper complexes in aqueous solution are reported. In addition to the di-glycine complex, well-known from EPR studies in the solid state, the existence of mono- and tri-glycine complexes is shown. The mean parameters of the spin Hamiltonian are determined as $\bar{g} = 2.148$, 2.125, 2.13 and $a = 51.4$, 62.5, $79.6 \cdot 10^{-4}$ cm^{-1} for Gly 1, Gly 2 and Gly 3, respectively. From spectra taken in the vitrous state, values of $g_{||} = 2.301$ and 2.251, $g_{\perp} = 2.072$ and 2.062, $A = 165.9$ and 187.5, $B = 9.1$ and $4.1 \cdot 10^{-4}$cm^{-1} are determined for Gly 1 and Gly 2. The variation in linewidth vs glycine concentration is established. Tumbling and spin-rotation correlation times are calculated.

1. Introduction

A considerable amount of work, dealing with the radiospectroscopy of glycine compounds, has hitherto been carried out at the Institute of Molecular Physics of the Polish Academy of Sciences in Poznań. Single crystals of glycine, triglycine sulphate, as well as triglycine fluoroberyllate, admixtured with the paramagnetic ions Cu^{2+} [1–4], Cr^{+3} [5, 6], and VO^{2+} [7], have been studied. The methods of electron and nuclear magnetic resonance made it possible to establish the structure, symmetry and orientation of the paramagnetic centre in the crystal, whereas temperature-dependent and high-pressure studies [8–10] yielded information concerning molecular motion.

The present paper is aimed at a study of glycine-copper complexes in aqueous solution, in particular at the determination of the various types of these complexes, at a comparison of the EPR spectral parameters of the complexes in aqueous solution and when rigidly fixed in the crystal lattice, and at the elucidation of the relaxation mechanisms.

2. Glycine-copper complexes

Glycine (Gly) can occur in solution in one of the following three forms: as an anion ($NH_2CH_2COO^-$), a "zwitter" ion ($NH_3^+CH_2COO^-$), or a cation ($NH_3^+CH_2COOH$). In solutions with $pH = 6.06$, glycine is in the isoelectric point and the over-all electric charge

* Address: Instytut Fizyki Molekularnej, PAN, Smoluchowskiego 17/19, 60-179 Poznań, Poland.

of the glycine ions is zero. Glycine then tends equally to go over into the cationic and anionic form. The anion arises at $pH > 6.06$, i. e., in a neutral or basic medium in accordance with the reaction

$$NH_3^+CH_2COO^- + H_2O \xrightarrow{nH=7} NH_2CH_2COO^- + H_3O^+ \quad (1)$$

or

$$NH_3^+CH_2COO^- + OH^- \xrightarrow{pH>7} NH_2CH_2COO^- + H_2O. \quad (2)$$

In such solutions, the addition of glycine lowers the *pH*-value as the number of OH^--groups decreases (in accordance with reaction (2)) or hydronium ions H_3O^+ are formed (in accordance with reaction (1)).

In a sufficiently acidic solution ($pH < 6.06$), a proton becomes bonded to glycine giving rise to the glycine cation

$$NH_3^+CH_2COO^- + H_3O^+ \xrightarrow{pH<6.06} NH_3^+CH_2COOH + H_2O. \quad (3)$$

This, in turn, leads to a decrease in acidity and an increase in *pH*. In our experiments, the *pH*-value varied as a function of the glycine concentration obeying reaction (3) (see Fig. 1a). The distilled water used was slightly acidic owing to the formation of carbonic acid from atmospheric carbon dioxide ($pH \simeq 5.6$–6.0).

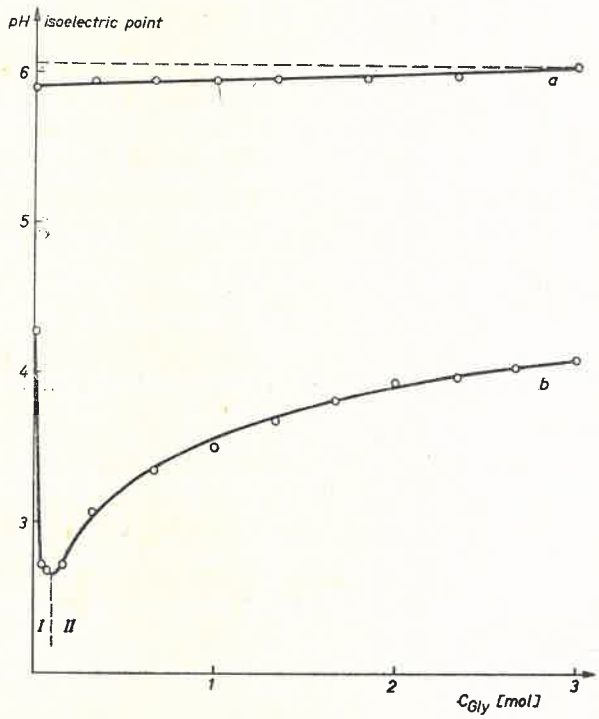

Fig. 1. *pH* of the solution vs glycine concentration: *a* — without Cu^{+2}; *b* — with 0.05 mole Cu^{+2}

The addition of copper ions Cu^{2+} to an aqueous solution of glycine (we applied copper sulphate $CuSO_4 \cdot 5H_2O$ for this purpose) leads to the formation of glycine-copper complexes according to the reaction

$$Cu^{+2} + xNH_3^+CH_2COO^- \rightarrow CuGly_x^{+(2-x)} + xH^+. \tag{4}$$

As the complexes arise, the solution becomes intensely blue, of a colour specific to copper--nitrogen compounds ($\lambda_{max} = 630$ mμ). The amino-copper ion $Cu(NH_3)_4^{+2}$ is of a similar colour. In addition to the hexahydrous copper complex $Cu(H_2O)_6^{+2}$, glycine-copper complexes of the following three types can occur in solution

$$x = 1 \quad [Cu(H_2O)_4Gly]^{+1},$$

$$x = 2 \quad Cu(H_2O)_2Gly_2,$$

$$x = 3 \quad CuGly_3.$$

The formation of glycine-copper complexes involves the setting free of protons and thus a lowering of *pH*. This is shown in Fig. 1b, where the first region of glycine concentrations (I) corresponds to the formation of glycine-copper complexes in accordance with reaction (4), whereas at higher glycine concentrations (region II) on observes a transition of the "zwitter" ion into the cation in accordance with reaction (3).

3. EPR spectra of copper complexes in aqueous solutions

The EPR spectrum of copper complexes consists essentially of four hyperfine structure (HFS) lines, due to interaction between the unpaired electron and copper nucleus ($^{63}I_{Cu} = {}^{65}I_{Cu} = 3/2$). Depending on the symmetry and structure of the complex, the following, fundamental parameters of the spin Hamiltonian vary: the spectroscopic splitting factor g, the HFS constant A, and the linewidth ΔH. These parameters when available, help to determine the type of complex. In the solid state, anisotropy investigation of the spectrum enables one to determine the tensors $\vec{\vec{A}}$ and $\vec{\vec{g}}$ as well as their principal values (A_z, A_x, A_y and g_z, g_x, g_y). In the majority of cases, the copper ion occurs in an axially-symmetric surroundings, causing a reduction to four in the number of unknown parameters ($A = A_z$, $B = A_x = A_y$ and $g_{||} = g_z$, $g_\perp = g_x = g_y$).

In the liquid the copper complexes are involved in random Brownian motion. Their positions, as well as the angles subtended by their electric axis and the external magnetic field, vary all the time. As shown by McConnell [11], the spin Hamiltonian can be resolved into two terms

$$\check{\mathcal{H}} = \check{\mathcal{H}}_0 + \check{\mathcal{H}}(t). \tag{5}$$

The isotropic terms $\check{\mathcal{H}}_0$ is time-independent

$$\check{\mathcal{H}}_0 = \bar{g}\beta H S_z I_z + a S_z I_z \tag{6}$$

with

$$\bar{g} = \tfrac{1}{3}(g_{||} + 2g_\perp) \quad \text{and} \quad a = \tfrac{1}{3}(A + 2B).$$

The second term of the Hamiltonian is of the form

$$\begin{aligned}\check{\mathscr{H}}(t) = {} & (\Delta g\beta H + bI_z)(\cos^2\theta - \tfrac{1}{3})S_z + \tfrac{1}{2}(\Delta g\beta H + bI_z)\sin\theta\cos\theta(S_+e^{-i\varphi} + S_-e^{+i\varphi}) \\ & -\tfrac{1}{4}b(\cos^2\theta - \tfrac{1}{3})(S_+I_- + S_-I_+) + \tfrac{1}{4}b\sin^2\theta(I_+S_+e^{-2i\varphi} + I_-S_-e^{+2i\varphi}) \\ & +\tfrac{1}{4}b\sin\theta\cos\theta(I_+e^{-i\varphi} + I_-e^{+i\varphi})S_z \end{aligned} \tag{7}$$

where $\Delta g = g_{||} - g_{\perp}$ and $b = A - B$. Here, dependence on time is inherent in the variability of the polar angle θ and azimuthal angle φ as a result of rotations of the complex, involved in Brownian motion.

The centre of gravity of each of the four HFS lines is to be obtained from the eigenvalues of the isotropic Hamiltonian $\check{\mathscr{H}}_0$. The term $\check{\mathscr{H}}(t)$ causes a broadening of the components of the spectrum. This broadening is a function of the correlation time τ_c defining the lapse of time necessary for a rotation of the complex by an angle of 2/3 radians on an average (rotation), or for a doubling of the distance between mutually interacting complexes (translation).

For sufficiently short times τ_c, the term $\check{\mathscr{H}}(t)$ vanishes on averaging. The EPR spectrum then exhibits narrow HFS components with equal amplitudes. If this benifical averaging fails to take place, one observes a spectrum of diffuse structure. Typically, as a result of bad averaging, one obtains a spectrum with unequal widths of the HFS components.

If the tensors $\overrightarrow{\overrightarrow{g}}$ and $\overrightarrow{\overrightarrow{A}}$ have the same symmetry and coinciding principal axes, the HFS line-widths depend, according to the theory of McConnell [11], on the nuclear magnetic quantum number m_I as follows

$$\Delta H^{\mathrm{T}} = C_1 + C_2 m_I + C_3 m_I^2. \tag{8}$$

The coefficients C_i of Eq. (8) are to be evaluated from the following expressions [12]

$$C_1 = \frac{\pi}{120}10^{-8}\frac{hc^2}{g\beta}\tau_c^{\mathrm{T}}\left\{8(4+3\alpha)(\overrightarrow{\overrightarrow{g}}:\overrightarrow{\overrightarrow{g}})\frac{10^{26}\nu^2}{g^2c^2} + 15(3+7\alpha)(\overrightarrow{\overrightarrow{A}}:\overrightarrow{\overrightarrow{A}})\right\}, \tag{9}$$

$$C_2 = \frac{2\pi}{15}10^5\frac{h\nu c}{g^2\beta}\tau_c^{\mathrm{T}}(4+3\alpha)(\overrightarrow{\overrightarrow{g}}:\overrightarrow{\overrightarrow{A}}), \tag{10}$$

$$C_3 = \frac{\pi}{30}10^{-8}\frac{hc^2}{g\beta}\tau_c^{\mathrm{T}}(5-\alpha)(\overrightarrow{\overrightarrow{A}}:\overrightarrow{\overrightarrow{A}}) \tag{11}$$

where $\alpha = (1+4\pi^2\nu^2\tau_c^{\mathrm{T}2}\cdot 10^{18})^{-1}\cdot A$ and ν are expressed in 10^{-4} cm^{-1} and GHz, respectively.

In the axial case, the internal products of the anisotropic tensors $\overrightarrow{\overrightarrow{A}}$ and $\overrightarrow{\overrightarrow{g}}$ take the form

$$\begin{aligned}(\overrightarrow{\overrightarrow{g}}:\overrightarrow{\overrightarrow{g}}) &= 2/3(g_{||} - g_{\perp})^2, \\ (\overrightarrow{\overrightarrow{A}}:\overrightarrow{\overrightarrow{A}}) &= 2/3(A-B)^2, \\ (\overrightarrow{\overrightarrow{g}}:\overrightarrow{\overrightarrow{A}}) &= 2/3(A-B)(g_{||} - g_{\perp}),\end{aligned} \tag{12}$$

On insertion of the quantities (12) and elementary constants into Eq. (9)–(11), one obtains

$$C_1 = \frac{10^{11}\tau_c^T}{g}\left[0.9969(4+3\alpha)\left(\frac{g_\parallel - g_\perp}{g}\right)^2 \nu^2 + 16.8105 \cdot 10^{-6}(3+7\alpha)(A-B)^2\right], \tag{13a}$$

$$C_2 = 0.0060\,\frac{10^{11}\tau_c^T \nu}{g^2}(4+3\alpha)(g_\parallel - g_\perp)(A-B), \tag{13b}$$

$$C_3 = 4.4828\,\frac{10^5\tau_c^T}{g}(5-\alpha)(A-B)^2. \tag{13c}$$

McConnell's tumbling mechanism of motion of the complex leads to proportionality between the linewidth and relaxation time τ_c^T. With regard to the dependence

$$\tau_c = \frac{4\pi\eta a_0^3}{3KT} \tag{14}$$

the linewidth is found to be proportional to the viscosity of the medium. McConnell's mechanism, related to rotation of the stable complex with anisotropic EPR parameters in the magnetic field, is not the only source of linewidth. The linewidth can moreover undergo modifications as a result of the relaxation originating in spin-rotation interaction. The spin-rotation relaxation time τ_{RS} is related to deceleration and acceleration of rotation of the paramagnetic complex and with interaction between the magnetic field thus arising and the moments of neighbouring nuclei and electrons. According to the theory of Atkins-Kivelson [19], one has for spin $S = 1/2$

$$T_{RS}^{-1} = \frac{1}{12\pi a_0^3}(\vec{\vec{g}} : \vec{\vec{g}})\frac{KT}{\eta}. \tag{15}$$

On insertion of (12) and (14) into Eq. (15), we obtain

$$\Delta H^{RS} = \frac{1}{27\pi}\frac{h}{g\beta}(g_\parallel - g_\perp)^2 \frac{1}{\tau_c^{RS}}. \tag{16}$$

The above linewidth is inversely proportional to the correlation time τ_c^{RS} and thus to the viscosity. On omission of the relaxation time T_1, the linewidth becomes equal to the sum of the McConnell and Kivelson contributions

$$\Delta H_L = \Delta H^T + \Delta H^{RS}. \tag{17}$$

The total linewidth ΔH_L is the half-width of a Lorentzian line.

4. EPR spectra — experimental

We studied the ternary system $H_2O : Cu^{+2}$: Gly versus the glycine concentration. In all cases, 0.05 mole of Cu^{+2} was taken (in the form of copper sulphate $CuSO_4 \cdot 5H_2O$), corresponding to the maximal amount of Cu^{+2} ions not causing dipole-dipole deformation

of the spectrum. The glycine concentration varied from 0 to 3 mole, i. e., up to saturation at room temperature. A microwave EPR spectrometer, operating at 9.3 GHz with 130 kHz magnetic field modulation, constructed in Wrocław Technical University, was used. For all the complexes, a strong dependence of the linewidths on the quantum number m_I was

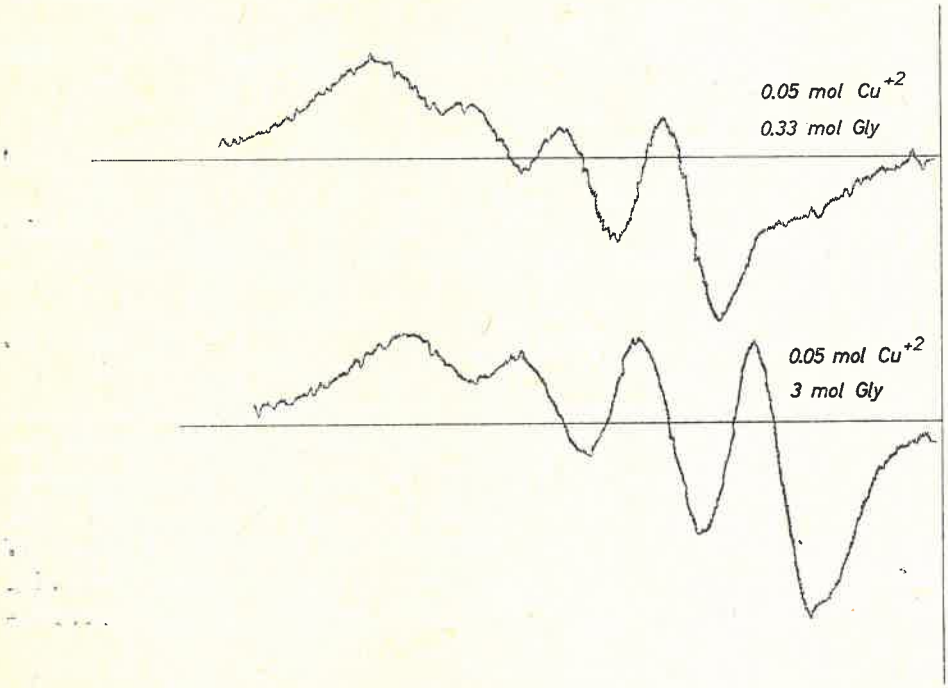

Fig. 2. EPR spectrum of aqueous solutions with 0.05 mole Cu^{+2} and (a) 0.33 mole Gly, (b)3 mole Gly

observed for the spectra of the solutions. Fig. 2 shows spectra of aqueous Cu: Gly solutions for the two glycine concentrations 0.33 mole and 3 mole.

The spectrum of glycine-copper complexes is not readily decipherable for two reasons. Its interpretation is obscured, firstly, by the overlapping of components originating in complexes with different parameters and, secondly, by the varying width of the individual lines. For the analysis of these highly complicated spectra, we had recourse to an electronic "ODRA 1013" computer. The experimental spectrum y'_{exp} was compared with the theoretical spectrum being the sum of the spectra of the three copper complexes:

$$y'_{\text{theor}} = \varepsilon + \varphi H + \sum_{l=1}^{3} \sum_{m_I=-3/2}^{+3/2} \frac{W^{(l)}[\Delta H_{\text{L}}^{(l)} - C_2^{(l)} m_I]\,[H - (m_I a^{(l)} + H_0^{(l)})]}{\{[\Delta H_{\text{L}}^{(l)} - C_2^{(l)} m_I]^2 + [H - (m_I a^{(l)} + H_0^{(l)})]^2\}^2}, \tag{18}$$

with: $W^{(l)}$ — the total amplitude of the line, proportional to the number of complexes of the l-th type; $\Delta H_l = \frac{\sqrt{3}}{2} \Delta H_{\max}$ — the Lorentz half-width; $H_0^{(l)}$ — the position of the centre of the l-th spectrum.

The quantities ε and φH denote, respectively, the mean offset and linear drift terms, and eliminate errors in recording. The calculations consisted in a variational adjustment, for each of the three complexes, of the parameters occuring in Eq. (18) so as to minimalize the divergences between the experimental and theoretical spectra. The analysis was performed on 35 points, equidistant on the scale of magnetic field strength H, until the error fell to less than 10 per cent. Error was taken as $\sum_{i=1}^{35} |\Delta y_i'| / \sum_{i=1}^{35} |y_i'| \cdot 100\%$. Fig. 3 shows an example of this adjustment of the theoretical spectrum to the experimental one (the small circles denote the amplitude values of the line calculated from Eq. (18)).

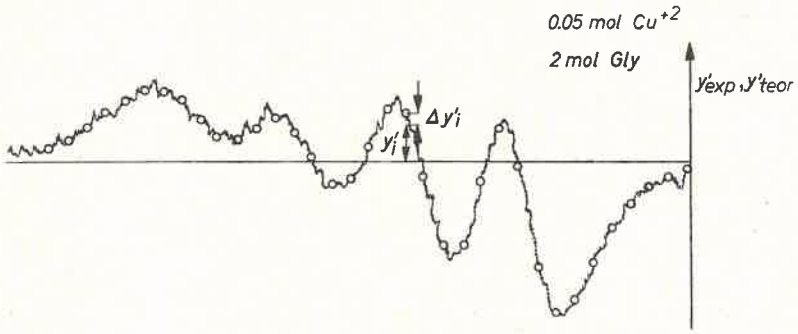

Fig. 3. Example showing adjustment of the theoretical spectrum to the experimental one, for $C_{Gly} = 2$ mole. The dots give the amplitudes of the theoretical spectrum

Our analysis of the results points to the presence of four complexes: $Cu(H_2O)_6$, $Cu(H_2O)_4Gly$, $Cu(H_2O)_2Gly_2$ and $CuGly_3$ in solution. We denote them, respectively, as Gly 0, Gly 1, Gly 2 and Gly 3. Up to a glycine concentration of 1.33 mole spectra of Gly 0, Gly 1 and Gly 2 were simulated: henceforth, with regard to the negligible amplitude of Gly O, we began to take into account the complex Gly 3. On the assumption that all the copper ions yield an EPR spectrum, we calculated the concentration of the l-th complex as $C_{comp}^{(l)} = C_{Cu} W^{(l)} / \sum_i W^{(l)}$.

The increase in glycine concentration is accompanied by a vanishing of free, hydrated copper ions (Gly 0) in favour of glycine-copper complexes (Fig. 4). The addition of 0.33 mole of glycine lowers the concentration of centres of the type Gly 0 by about 15 per cent. Simultaneously, complexes Gly 1 and Gly 2 appear. The initial predominance of the mono-glycinic centre weakens, and upwards of a concentration of 0.7 mole Gly the di-glycinic complex predominates. Upwards of 1.7 mole Gly the equilibrium $C_{Gly2}:C_{Gly1}:C_{Gly3} = 6:\ 1.5:\ 1$ sets in between the different complexes in the solution.

The linewidth $\Delta H_L^{(l)}$ decreases as the number of glycine molecules bonded to the central ion increases. However, the shape of the glycine concentrational dependence of the linewidth (Fig. 5) i. e. the latter's dependence on the macroscopic viscosity of the solution points to different contributions from the two above described relaxation mechanisms. In the case of the complexes Gly 0 and Gly 1, the chief role belongs to the tumbling relaxation mechanism (the linewidth increases with growing glycine concentration), whereas in

that of Gly 2 and Gly 3 the linewidth decreases with increasing viscosities (as suggested by the spin-rotation relaxation mechanism).

The portion of the linewidth dependent on the magnetic quantum number m_I varies also with increasing glycine concentrations (Fig. 6). It increases with increasing viscosity but decreases from one complex to another as successive glycine molecules are bonded to

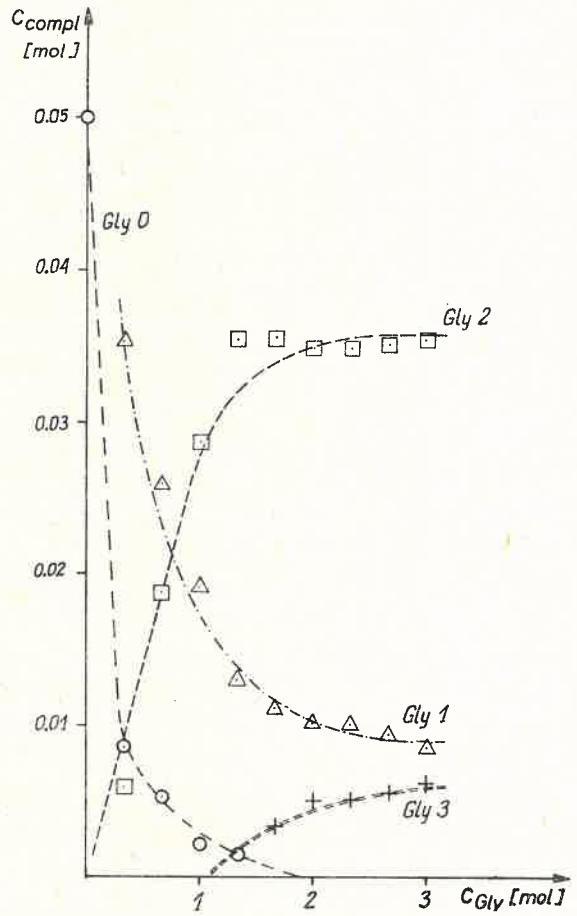

Fig. 4. Concentrations of the copper complexes vs the glycine concentration

the copper ion. Since the parameter C_2 is proportional to the tumbling correlation time, τ_C^T decreases on transition from Gly 1 to Gly 3.

The other parameters of the spectrum — the splitting factor $\bar{g}$ and HFS constant a exhibit no dependence on the glycine concentration. Their values are given in Table I.

Noteworthy is the increase in a and decrease in $\bar{g}$ as the number of glycines in the complex increases. Both parameters are related to the ionicity of the central ion-ligand bond. According to the Kivelson-Neiman graph [20], an increase in the number of glycines entails an increase in covalence of the bond, from almost ionic Gly 0 to predominantly molecularly bonded Gly 3. The HFS constant a is inversely proportional to the spin density

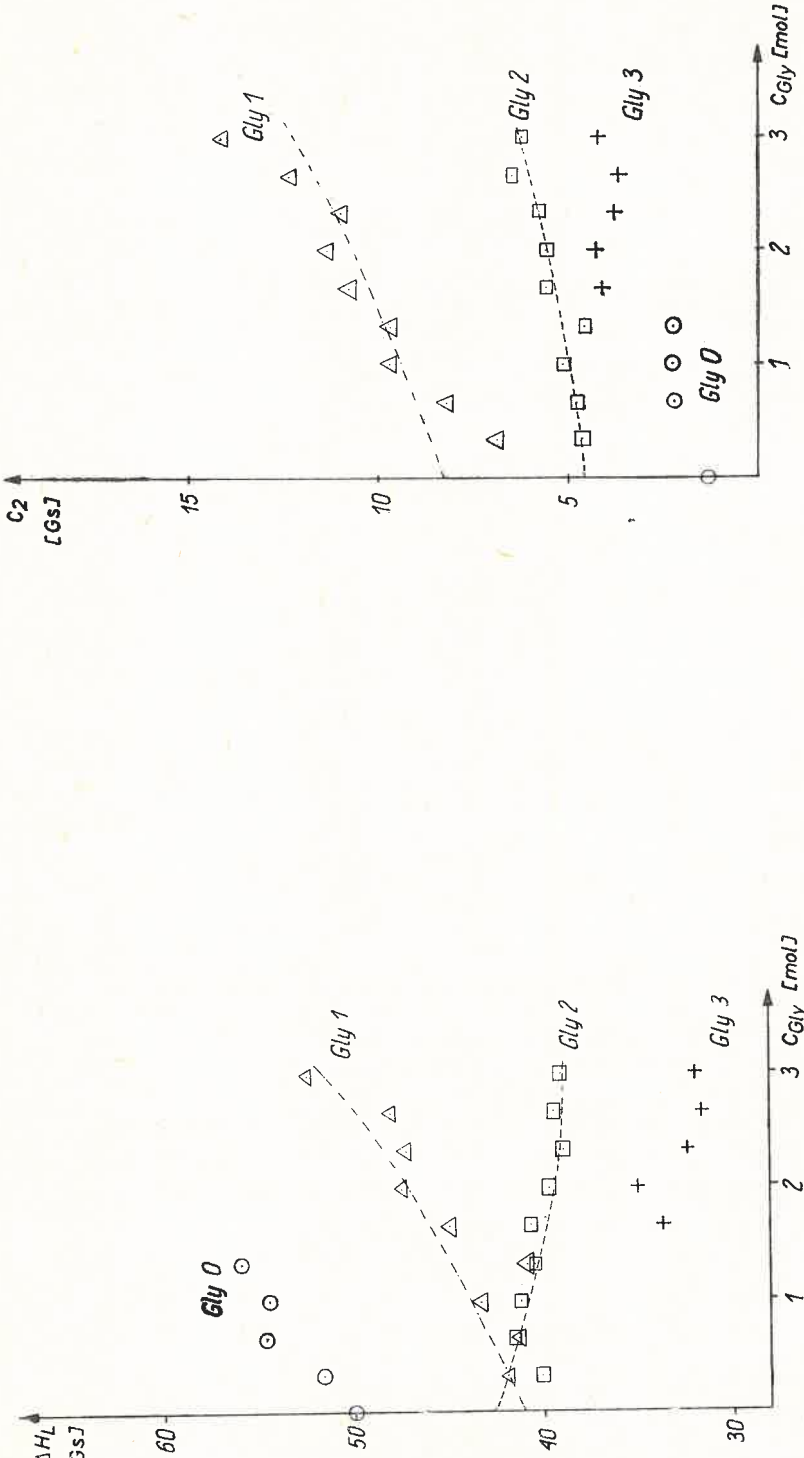

Fig. 5

Fig. 6

Fig. 5. Linewidth ΔH_L vs glycine concentration. The dashed lines show the theoretical ΔH_L curve for correlation times equalling $\tau^T_{c_0} = 4.38$; $\tau^{RS}_{c_0} = 2.07 \cdot 10^{-11}$ s for Gly 1 and $\tau^T_{c_0} = 2.01$ and $\tau^{RS}_{c_0} = 0.58 \cdot 10^{-11}$ s for Gly 2

Fig. 6. Parametr C_2 vs the glycine concentration. The theoretical curves are plotted for the $\tau^T_{c_0}$ — values of Fig. 5

TABLE I

Type of complex	$\bar{g}$	$a(10^{-4}\text{cm}^{-1})$
Gly 0	2.179	33.9
Gly 1	2.1480	51.4
Gly 2	2.1257	62.5
Gly 3	2.13	79.6

value α'^2 on the ligand of the complex. Thus, for Gly 0, α'^2 is large and decreases as more and more glycines are bonded to the copper ion. This is due to the decrease in linewidth with increasing covalency of the bond (as confirmed in the present paper), as well as the decrease in HFS constant, which originates in the nuclei of the ligand. Fig. 7 represents

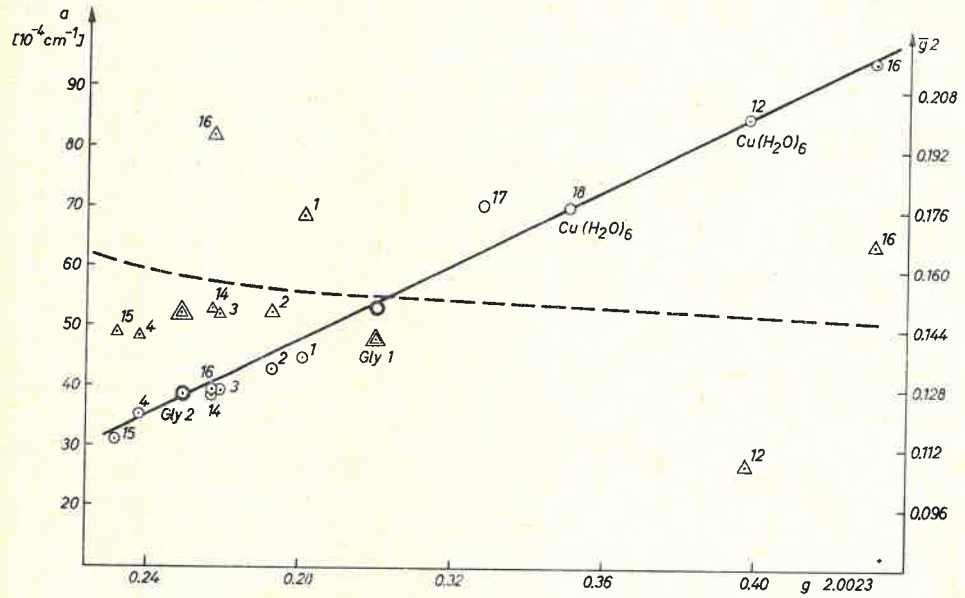

Fig. 7. Kivelson–Neiman graph for glycine-copper complexes. ○ — $\bar{g}$–2; △ — a. Indices give the Reference number in the list at the end of this paper

the Kivelson-Neiman graph for glycine-copper complexes. The indices at the experimental points stand for the Reference in the list attached. The circles and triangles denote, respectively, the dependence of $\bar{g}$–2 and a vs $g_{||} - 2.0023$. The double circles and triangles represent complexes Gly 1 and Gly 2, studied in this paper. The data sub 12 and 18 are for hexahydrous complexes of copper.

5. *Spectrum of the frozen (vitrous) solution*

In order to evaluate the correlation times τ_c, the parameters $g_{||}$, $g_{\perp}$, A and B have to be available numerically, in accordance with Eqs (13), (16) and (17). We determined these parameters from the spectrum of a frozen solution with 0.05 mole Cu^{2} and 3 mole Gly

(Fig. 8). The weak field portion of the spectrum contained three well apparent pairs of lines, corresponding to the parallel orientation of two complexes: *a* with a larger and *b* with a lesser amplitude. The fourth lines for this orientation were obliterated by the unresolved structure of the perpendicular orientation with a strongly marked, additional

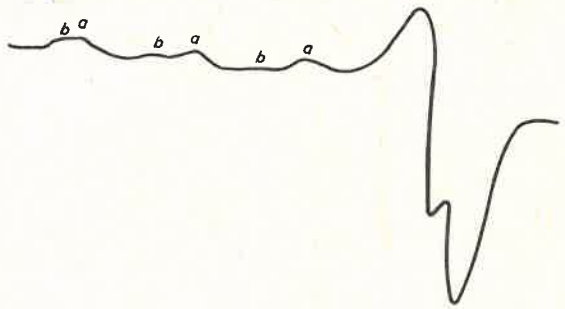

Fig. 8. EPR spectrum of glycine-copper complexes in a frozen (vitrous) solution containing 0.05 mole Cu^{+2} and 3 mole Gly. Temperature −77 K. *a* = Gly 2; *b* — Gly 1

signal. The amplitude of the spectrum as well as the averaged parameters $\bar{g}_{vitr}$ and a_{vitr} indicate that *a* corresponds to the complex Gly 2 and *b* to Gly 1. The results of our study of the frozen solutions and of their comparison with the liquid state parameters are given in Table II.

TABLE II

Type of complex	$g_{\|\|}$	$g_\perp$	$\bar{g}_{vitr}$	A	B	a_{vitr}	$\bar{g}$	a
Gly 1 = *b*	2.301_1	2.072_3	2.148_5	165.9	9.1	57.7	2.148_0	51.4
Gly 2 = *a*	2.251_3	2.062_0	2.125_1	187.5	4.1	61.8	2.125_7	62.5

6. *Evaluation of the correlation times*

With the parameters $g_{||}$, $g_\perp$, A, B available, we proceeded to evaluate the correlation times τ_c^T and τ_c^{RS}. With regard to the Landolt-Börnstein data [13], we assumed the viscosity of aqueous solutions of glycine to vary in accordance with the formula

$$\eta/\eta_0 = 1+0.14193C_{Gly}+0.013048C_{Gly}^2 \qquad (19)$$

where η_0 is the viscosity of water. No influence of the copper ions and complexes on the viscosity was taken into consideration. Correlation times $\tau_{c0} = \dfrac{\tau_c}{\eta/\eta_0}$, extrapolated to zero glycine concentration, were determined.

The correlation time τ_{c0}^T was determined from the dependence of C_2 on the glycine concentration, since this parameter is related to the McConnell mechanism only. The best adjustment of the theoretical curve (the dashed line in Fig. 6) to the experimental points

was achieved with $\tau_{c0}^{T} = 4.30 \cdot 10^{-11}$ s for Gly 1 and $2.01 \cdot 10^{-11}$ s for Gly 2. In Fig. 6, the variation of C_2 for Gly 1 is seen to be but slightly steeper than predicted by the theory, whereas for Gly 2 agreement between theory and experiment is excellent.

The correlation time τ_{c0}^{RS} was determined from the shape of $\Delta H_L = f(C_{Gly})$. In order to achieve satisfactory agreement, it was necessary to increase the contribution of tumbling to the linewidth, in accordance with the formula

$$\Delta H_L = 2.6\Delta H^T + \Delta H^{RS}. \tag{20}$$

Calculated on this assumption the correlation times τ_{c0}^{RS} amount to $2.07 \cdot 10^{-11}$ s for Gly 1 and $0.56 \cdot 10^{-11}$ s for Gly 2. The theoretical curve for the two complexes is shown in Fig. 5 (dashed line). For a lack of the complete EPR parameters for Gly 3, we could but perform a rough assessment of the two correlation times. The tumbling correlation time has to be less than the times τ_{c0}^{T} for Gly 1 and Gly 2, and amounts to $1.8 \cdot 10^{-11}$ s approximately, whereas τ_{c0}^{RS} is comparable with the time τ_{c0}^{RS} for Gly 2, and is evaluated as $0.5 \cdot 10^{-11}$ s. Table III contains the correlation times for the glycine complexes.

TABLE III

Type of complex	$\tau_{c0}^{T} \cdot 10^{11}$s	$\tau_{c0}^{RS} \cdot 10^{11}$ s
Gly 1	4.38	2.07
Gly 2	2.01	0.56
Gly 3	~1.8	~0.5

By Eq. (13) and knowing the correlation times τ_{c0}^{T}, we evaluated the parameter C_3 as amounting to about ~ 1 Gs for Gly 1 and ~ 0.7 Gs for Gly 2. Consequently, in the EPR spectrum of the complex Gly 1, the outer lines are additionally broadened by about ~ 2 Gs and the inner ones by ~0.3 Gs. Likewise, for Gly 2, the broadening amounts to about 1.5 and 0.2 Gs, respectively. Thus, the omission of this contribution in our analysis of the spectrum was fully justified with regard to the linewidth, which is of the order of 30–50 Gs.

7. *Discussion*

The complexes are endowed with their kinetic energy as the result of collisions with molecules of water. Let us assume that, irrespective of the type of complex, a constant portion of this energy is transformed into kinetic energy of rotational motion, $1/2\,\omega_{c0}^2 I$. Since as the tumbling reorientation time τ_{c0}^{T} is halved as we go over from Gly 1 to Gly 2, the angular velocity ω_{c0} has to be doubled. Conservation of constant kinetic energy requires that the moment of inertia of Gly 2 be one quarter that of Gly 1. Now, since the spin-rotation correlation time τ_{c0}^{RS} is proportional to the moment of inertia I, it too has to decrease 4-fold. This is corroborated by the experimental results. On the other hand, the transition from Gly 1 to Gly 2 consist in the replacement of 2 water molecules by 1 glycine molecule of a mass double that of the 2 waters. This increases by a factor of 1.34

the moment of inertia, calculated with respect to the z-axis of the complex. The discrepancy can be explained by changes in the hydration shell of the complex. In the case of Gly 1 the latter is large owing to the un-screened Cu^{+2} ion and the presence of charge. Transition to Gly 2 entails screening of Cu^{+2} by the other glycine anion and compensation of the ionic charge, thus lowering the electrostatic forces keeping the hydration sphere together. This, in turn, lowers the moment of inertia.

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