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B.N. Misra, R. Kripal. Study of ESR absorption and bonding character of copper (II) complex with L-Hydroxyproline. *Revue de Physique Appliquée*, 1981, 16 (8), pp.411-417. 10.1051/rphysap:01981001608041100 . jpa-00244934

**HAL Id: jpa-00244934**

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Submitted on 4 Feb 2008

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Classification  
Physics Abstracts  
33.30

## Study of ESR absorption and bonding character of copper (II) complex with L-Hydroxyproline

B. N. Misra and R. Kripal

Department of Physics, University of Allahabad, Allahabad, India

(Reçu le 29 septembre 1980, révisé le 2 février et le 24 avril 1981, accepté le 27 avril 1981)

**Résumé.** — L'étude par EPR du complexe de cuivre (II) et de l'acide aminé L-Hydroxyproline a été réalisée sous différentes formes : polycristalline, verre en solution. Des mesures d'absorption optique et de susceptibilité magnétique ont été faites et divers paramètres magnétiques et non magnétiques en ont été déduits. Ils ont été utilisés pour déterminer les paramètres de liaison en se fondant sur les déductions théoriques de Roberts et Koski. La largeur hyperfine de chaque raie a été mesurée et les résultats ainsi obtenus ont été interprétés par la théorie de Kivelson sur les largeurs de raie en solution. La susceptibilité magnétique du complexe a ainsi été calculée théoriquement. Les résultats obtenus par les trois types de mesures décrits précédemment sont correctement corrélés.

**Abstract.** — The ESR study of the copper (II) complex with L-Hydroxyproline amino acid has been carried out in three different forms, namely polycrystalline, glass and solution states. The optical absorption and magnetic susceptibility measurements have also been performed. Various magnetic and non-magnetic parameters have been evaluated. Further, these parameters have been used to determine the bonding parameters based on the theoretical deduction of Roberts and Koski. Hyperfine linewidth of each line has been measured and the data thus obtained have been interpreted on the basis of Kivelson's theory of linewidth in solution. The magnetic susceptibility of the complex has also been theoretically calculated. The data obtained from all the three measurements described above have been found to justify one and the other.

**1. Introduction.** — The properties of copper compounds, both in the doped inorganic crystals and in organic complexes, have been studied extensively by electron spin resonance and optical spectroscopy [1-4]. In the present investigation, ESR, optical absorption and magnetic susceptibility measurements have been carried out to obtain important information about the magnetic and non-magnetic interactions as well as about the nature of chemical bonding in a copper amino acid complex. The information drawn in this way is of particular importance in the study of living organisms as amino acids and their compounds are constituents of them.

In general, the ESR studies are performed on magnetically dilute single crystals but it is not always possible to make such crystals, and therefore one is limited to the use of samples having random orientation of the paramagnetic centres. Here also, due to

lack of suitable single crystals, the ESR parameters have been evaluated from a combination of polycrystalline, glass and solution state ESR spectrum. Various ESR linewidth theories [5-9] have been used to determine different linewidth parameters. The optical absorption study of the complex has been performed in order to decide the symmetry and finally the ground state of the paramagnetic ion whereas the magnetic susceptibility study of the complex has been done to justify the interpretation of ESR data.

**2. Experimental details.** — **2.1 SAMPLE PREPARATION.** — The copper (II) complex with L-Hydroxyproline [10] was prepared by earlier method. The plate type blue crystals were obtained with the following composition :

Found : C, 31.05 ; H, 5.04 ; N, 7.21 ; Cu, 16.67 % ; density, 1.52 g/cm<sup>3</sup>.

Calculated for



C, 31.79; H, 5.87; N, 7.41; Cu, 16.82%; molecular weight, 377.83.

**2.2 TECHNIQUE.** — Optical absorption study of the complex in aqueous solution has been done at Cary (Model-14) automatic recording spectrophotometer in the region  $13\,330\text{--}28\,570\text{ cm}^{-1}$ . A  $10^{-3}$  mol./l solution in pyrex capillary tube was used for the ESR study of the solution. The glass sample was prepared by dissolving the complex in a glycerine-water mixture having glycerine-to-water ratio of 3 : 2 and cooling it to 77 K in a quartz tube. The ESR measurements have been done on Varian X-band V4502-12, reflection type ESR spectrometer with 100 K c/s field modulation using a multipurpose V4531 ESR cavity. The magnetic field was measured by determination of the NMR frequency with a Hewlett Packard counter. The temperature control was effected with the aid of Varian temperature control unit. The magnetic susceptibility of the complex was measured by Faraday method with the help of single pan Mettler analytical balance (Model H16 GD) having a least count of  $10^{-5}$  g.

**3. Results and discussion.** — **3.1 OPTICAL ABSORPTION STUDY.** — The experimental optical absorption curve is a plot between optical density  $D$  versus wave number  $\sigma$  and is shown in figure 1 by solid line. The curve is found to be non-Gaussian which implies that it is not resulting from a single transition and is equivalent to a linear combination of two or three Gaussian curves. Such a Gaussian curve can be represented [11, 12] in terms of wave number  $\sigma$  as

$$\begin{aligned} \varepsilon &= \varepsilon_0 \exp - (\sigma - \sigma_0)^2 / \delta^2 \\ &= \varepsilon_0 2^{-(\sigma - \sigma_0)^2 / \delta^2} \end{aligned} \quad (1)$$

where  $\varepsilon_0$  is the maximum molar extinction coefficient at  $\sigma_0$  and  $\delta$  is the half width at half intensity points. As a combination of two or more Gaussian curves with different  $\delta$  and  $\sigma_0$  does not yield a simple expression, the curve analysis is performed employing trial

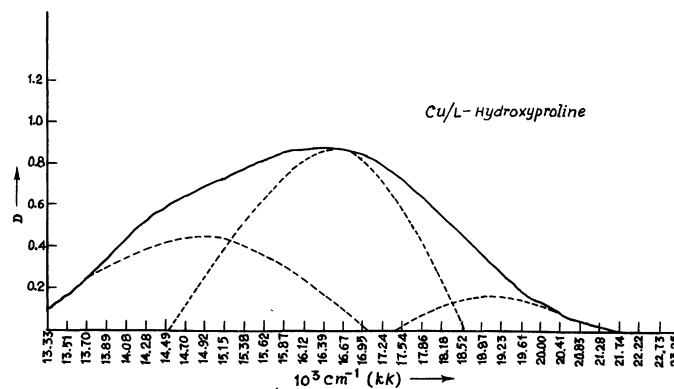


Fig. 1. — Experimental (—) and analysed (---) optical bands of Cu/L-Hydroxyproline in solution.

and error method [11, 12]. There are two such methods [11], namely Reflection in the Median Method and the Subtraction of the Extrapolated Background method. However, the first method has been used here for curve analysis which is as follows :

If one of the two sides of a curve is free from other band so that  $\delta$  can be determined, then the other side of the curve can be extrapolated with the same or slightly altered  $\delta$ . The other band can be found by subtracting the above approximately determined band from the experimental spectrum. Iteration of this procedure is done until the component bands have reasonable Gaussian shapes.

The heights  $\varepsilon_0$  and half width  $\delta$  of the component bands are generally uncertain sometimes to a factor of 5 while the individual maxima  $\sigma_0$  are much better determined, often with an accuracy of 0.1 kK [11].

The experimental spectrum in this case has been analysed into three Gaussian curves each of which corresponds to a single electronic transition. The analysed curves are shown by dotted lines. The measured parameters like line position  $\sigma$  ( $10^3\text{ cm}^{-1}$ ), half width  $\delta$  ( $10^3\text{ cm}^{-1}$ ), optical density  $D$ , molar extinction coefficient  $\varepsilon$  ( $\text{liter mol}^{-1}\text{ cm}^{-1}$ ) and oscillator strength  $f$  are given in table I.

The analysed bands are found to be of forbidden type ( $\varepsilon < 10^3$ ). This feature is supported by studies on crystals [13], aqueous solutions [14] and water-ammonia solutions [15] of copper (II) complexes.

Table I. — Parameters obtained from optical absorption study of the copper (II) complex.

		$\sigma$	$\delta$	$D$	$\varepsilon$	$f \times 10^4$	$\sigma_1/\sigma_2$
Cu/L-Hydroxyproline	Experimental band	16.36	2.11	0.90	32.4	6.29	
	Component bands						
	1	19.28	1.30	0.18	6.4	0.76	1.16
	2	16.57	1.30	0.89	32	3.82	
3	14.95	1.30	0.45	16.4	1.96		

This kind of spectrum is observed only for copper (II) complexes but not for the free ion which implies that the transitions take place between the different levels perturbed by the crystal field of the ligands. In this way, the analysed band positions convey important information regarding the symmetry of the ligand field around copper (II) ion. In octahedral symmetry of the field only one band is possible but in other fields like tetragonal, etc. the levels split and three bands are possible. Applying the theory of Hartmann and Ilse [16] and employing the point charge/dipole model, Bjerrum *et al.* [15] showed that  $\sigma_1/\sigma_2$  is 1 for octahedral symmetry. For copper nitrate in water and ammonia the ratio  $\sigma_1/\sigma_2$  has been found to be 1.33 and the structure is distorted octahedral. This ratio is slightly more than 1 for tetragonal symmetric complex [17]. Here, for the present complex, the ratio  $\sigma_1/\sigma_2$  is 1.16 and thus suggests a tetragonal symmetry of ligands around copper (II) ion. The inference drawn on the basis of the ratio  $\sigma_1/\sigma_2$  about the structure of the complex in many other cases has been found to agree well with the X-ray crystal structure data [17]. Therefore, the predicted symmetry of the complex in a way, is experimentally supported.

The cubic field splitting parameter  $\Delta$  has been estimated [18] by taking  $d_{x^2-y^2}$  as the ground state and the optical excitation energies as

$$\sigma_1 = d_{x^2-y^2} \rightarrow d_{xz,yz},$$

$$\sigma_2 = d_{x^2-y^2} \rightarrow d_{xy} \quad \text{and} \quad \sigma_3 = d_{x^2-y^2} \rightarrow d_{z^2}.$$

The value of  $\Delta$  determined here is 13.55 kK which is in agreement with the theoretical as well as experimental observations for similar complexes [17]. Hence the level arrangement as well as ground state assumed above is justified.

3.2 ESR STUDY. — The ESR spectra of the Cu/L-Hydroxyproline complex in polycrystalline, glass and solution states are shown in figure 2. For convenience the results will be discussed separately.

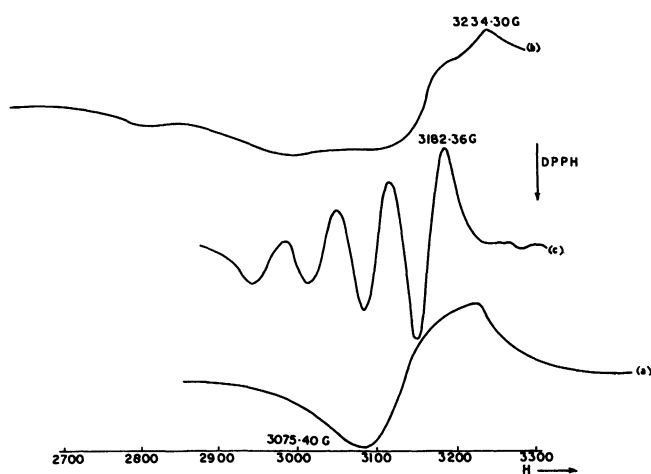


Fig. 2. — Experimental ESR spectra of Cu/L-Hydroxyproline in (a) polycrystalline, (b) glass, (c) solution states.

3.2.1 *Polycrystalline study.* — The polycrystalline spectrum has been analysed [4, 19] and the  $g$ -values have been determined. The line shape has been tested and found to be approximately Lorentzian. The peak-to-peak linewidth  $\Delta H_{pp}$  has been measured; it is larger than that of the pure copper salt [19]. The results thus obtained are shown in table II.

Table II. — Parameters obtained from polycrystalline sample study.

	$g_{\parallel}$	$g_{\perp}$	$\Delta g$	$g$	$\Delta H_{pp}$ (Gauss)
Cu/L-Hydroxyproline	2.168	2.076	0.092	2.107	135.92

From table II, it is seen that the observed  $g$ -values have been reduced in comparison with the pure copper compounds [19]. It indicates that the factors which control the  $g$ -values, namely, spin-orbit coupling constant  $\lambda$ , the energy difference between ground and excited levels  $\Delta E$  and nuclear and molecular magnetic fields might have changed in the complex. A small change in  $\Delta E$  will not affect  $g$  much and hence a reduction in effective  $\lambda$  due to bonding [20] is mainly responsible for the decrease in  $g$ -values. In this way, it is implied that the covalency has increased in the complex.

The change in linewidth is due mainly to the change in spin-lattice, dipole-dipole and exchange interactions [21]. In copper salt there is no great change of linewidth with temperature [21], which indicates that the spins are loosely coupled to lattice vibrations [17, 22] and thus spin-lattice interaction does not affect the width of the line to any marked extent. So the width of the line is controlled mainly by dipole-dipole and exchange interactions. It is obvious that after the complex formation, the crystal structure changes, the copper ions are kept apart as compared to their distance in pure copper salt and thus the dipolar and exchange interactions are reduced. But the decrease in exchange will be more important because of its exponential form [17] and so a broadening of the line is observed. Moreover, this decrease in exchange could not bring any change in the shape of the ESR line.

A definite and quantitative interpretation of the changes in linewidth can be produced using different linewidth theories [5-7, 23]. The calculated values of different parameters from above theories are given in table III.

It is observed from table III that  $(\Delta H_{1/2})_{exp}$  is smaller than  $(\Delta H_{1/2})_{cal}$  due to exchange coupling. The calculated values of dipolar width and exchange narrowing obtained from both the theories [6, 7] have reduced as compared to the pure copper salt. Further, the decrease in exchange frequency is more rapid than the dipolar width and therefore it is inferred that the reduction in exchange is the main cause of broadening of the line here.

Table III. — *Calculated values of linewidth, dipolar width and exchange frequency using different linewidth theories.*

Sample	Van Vleck Theory		Anderson-Weiss Theory		Kubo-Tomita Theory	
	Linewidth $(\Delta H_{1/2}^*)_{\text{exp}}$ $\times 10^{-9}$ (rad.s <sup>-1</sup> )	$(\Delta H_{1/2})_{\text{cal}}$ $\times 10^{-9}$ (rad.s <sup>-1</sup> )	Dipolar width $\omega_p^2 \times 10^{-18}$ (rad <sup>2</sup> .s <sup>-2</sup> )	Exchange freq. $\omega_e \times 10^{-9}$ (rad.s <sup>-1</sup> )	Dipolar width $\omega_{10}^2 \times 10^{-18}$ (rad <sup>2</sup> .s <sup>-2</sup> )	Exchange freq. $\omega_{20} \times 10^{-9}$ (rad.s <sup>-1</sup> )
CuCl <sub>2</sub> .2 H <sub>2</sub> O	1.39	12.89	44.85	34.18	31.95	101.77
Cu/L-Hydroxyproline	2.19	3.39	2.93	1.41	2.09	4.21

(\*)  $\Delta H_{1/2}$  = Half width at half power points =  $\sqrt{3} \Delta H_{pp}/2$  (For Lorentzian Shape).

3.2.2 *Glass study.* — The spin-Hamiltonian parameters from glass spectra can be obtained using the method developed by Kivelson and Neiman [24] and

applied by Vanngard and Assa [25]. The parameters obtained in this way are given in table IV.

Table IV. — *Parameters obtained from glass spectra* (\*).

	$g_{\parallel}$	$g_{\perp}$	$\Delta g$	$g$	$A_{\parallel}$ (10 <sup>9</sup> s <sup>-1</sup> )	$A_{\perp}$ (10 <sup>9</sup> s <sup>-1</sup> )
Cu/L-Hydroxyproline	2.254	2.056	0.198	2.122	2.904	0.469

(\*)  $\nu = 9\,131$  MHz.

The copper (II) complex with L-Hydroxyproline has been assumed to have square planar D<sub>4h</sub> symmetry and the 2s, 2p<sub>x</sub>, 2p<sub>y</sub> and 2p<sub>z</sub> orbitals of each of the four ligands are available to form molecular orbitals with the 3d orbitals of the central copper ion. The expressions for antibonding molecular orbitals have been given by Roberts and Koski [3] in terms of  $\alpha$  in-plane sigma bonding,  $\beta_1$  and  $\beta$  in-plane and out-of-plane pi bonding respectively. It has been discussed that  $\alpha^2$ ,  $\beta_1^2$  or  $\beta^2 = 1$  shows that the bond is hundred percent ionic and  $\alpha^2$ ,  $\beta_1^2$  or  $\beta^2 = 0.5$  represents hundred percent covalent character. The spin-Hamiltonian for Cu(II) in the field of D<sub>4h</sub> symmetry is given as

$$\mathcal{H} = \beta_0 [g_{\parallel} H_z S_z + g_{\perp} (H_x S_x + H_y S_y)] + A_{\parallel} S_z I_z + A_{\perp} (S_x I_x + S_y I_y) \quad (2)$$

in which the magnetic parameters,  $g_{\parallel}$ ,  $g_{\perp}$ ,  $A_{\parallel}$  and  $A_{\perp}$  are related [3] with the bonding parameters  $\alpha$ ,  $\alpha'$ ,  $\beta_1$  and  $\beta$ . Therefore, if  $g_{\parallel}$ ,  $g_{\perp}$ ,  $A_{\parallel}$  and  $A_{\perp}$  are known,  $\alpha$ ,  $\alpha'$ ,  $\beta_1$  and  $\beta$  can be evaluated from the expressions proposed [3]. The values of bonding parameters obtained are given in table V.

Table V. — *Bonding parameters for the copper (II) complex*

	$\alpha^2$	$\alpha'^2$	$\beta_1^2$	$\beta^2$
Cu/L-Hydroxyproline	0.73	0.30	0.95	0.95

It is seen from the expressions of bonding parameters proposed by Roberts and Koski [3] that the covalency decreases as  $g_{\parallel}$  and  $g_{\perp}$  increase or  $A_{\parallel}$  decreases. As the variation of  $g_{\parallel}$  is large from complex to complex and is an easily and precisely measurable parameter, it gives important information about copper ligand bonds. The  $g_{\parallel}$ -value has been found to be larger in case of glass than in the polycrystalline sample which indicates that the covalency is larger in polycrystalline sample than in its glass. From the data on bonding parameters in table V, it is observed that  $\alpha^2$  or  $\beta_1^2$  or  $\beta^2$  is greater than 0.5 but less than 1 which indicates that the bonding in the complex is fairly covalent. The same value for  $\beta_1^2$  and  $\beta^2$  indicates that the in-plane pi bonding is as covalent as the out-of-plane pi bonding. A fairly covalent nature of the complex is also in agreement with the optical study result of the same [24]. The bonding parameters obtained here are of the same order of magnitude, as found in other Cu(II) complexes of similar nature [4, 7, 24].

3.2.3 *Solution study.* — Kivelson [8], using theoretical deductions of Kubo and Tomita [7], developed the theory of linewidth in solutions under the assumption that the solutions are so dilute that the effect of dipolar and exchange interactions can be overlooked. The effect of only motional modulation of anisotropic  $g$  and  $A$  tensors on the linewidth has been considered. The spin-Hamiltonian is then given by

$$\mathcal{H}_{\text{spin}} = \mathcal{H}^{(0)} + \mathcal{H}^{(1)} + \bar{F}(t) \quad (3)$$

where

$$\begin{aligned}\mathcal{H}^{(0)} &= g_0 \beta_0 S_z H \\ \mathcal{H}^{(1)} &= \hbar a I_z S_z + \frac{1}{2} a \hbar [\bar{I}^+ \bar{S}^- - \bar{I}^- \bar{S}^+] \\ g_0 &= \frac{1}{3}(g_x + g_y + g_z) \\ a &= \frac{1}{3}(A_x + A_y + A_z)\end{aligned}$$

$F(t)$  is the time dependent part of the Hamiltonian and depends on the anisotropy of  $g$  and  $A$ . Assuming

that the spectral lines are well resolved, the magnetic field is strong so that the Zeeman term is the largest term in energy and the lineshapes are Lorentzian, Wilson and Kivelson [26] have shown that the linewidth

$$T_2^{-1} = A + BM + CM^2 + DM^3 \quad (4)$$

where the linewidth parameters  $A$ ,  $B$ ,  $C$  and  $D$  for the copper complex are given as

$$\begin{aligned}A/\tau_R &= \frac{1}{45} (\Delta\gamma H_0)^2 (4 + 3u) + \frac{1}{40} b^2 I(I+1) (3 + 7u) - \frac{1}{8} b^2 I(I+1) (a/\omega_0) uf - \frac{1}{30} \Delta\gamma H_0 b I(I+1) \times \\ &\quad \times (a/\omega_0) (1 + u) \\ B/\tau_R &= \frac{1}{15} (b \Delta\gamma H_0) (4 + 3u) - \frac{2}{45} (\Delta\gamma H_0)^2 (4 + 3u + 3uf) (a/\omega_0) - \frac{1}{20} b^2 I(I+1) (a/\omega_0) \times \\ &\quad \times (4 + 3u + 7uf) + \frac{1}{40} b^2 (a/\omega_0) (3 + 2u) [2I(I+1) - 1] \\ C/\tau_R &= \frac{b^2}{40} (5 - u) + \frac{1}{8} b^2 (a/\omega_0) uf - \frac{1}{30} (\Delta\gamma b H_0) (a/\omega_0) (7 + 5u + 12uf) \\ D/\tau_R &= \left(\frac{1}{20}\right) b^2 (a/\omega_0) (1 + u + uf).\end{aligned} \quad (5)$$

In above expressions

$$\begin{aligned}u &= 1 + \omega_0^2 \tau_R^2, \quad f = \omega_0^2 \tau_R^2 u, \quad \tau_R = \frac{4}{3} \pi r^3 \frac{\eta}{kT} \\ b &= \frac{2}{3}(A_{\parallel} - A_{\perp}) \text{ rad/s.} \\ \Delta\gamma &= \beta_0 \Delta g/\hbar, \quad \Delta g = g_{\parallel} - g_{\perp}.\end{aligned}$$

Here  $\omega_0$  is the microwave frequency in rad./s,  $\eta$  is the viscosity of the solution and  $r$ , the molecular radius of the equivalent rotating sphere in the solution. Equation (4) does not satisfy the experimental observations and has been modified as

$$T_2^{-1} = A + A' + BM + CM^2 + DM^3 \quad (6)$$

where  $A'$  is the residual linewidth due to unspecified mechanisms. The spin-rotational relaxation mechanism has been found to be the most important of these mechanisms. Atkins and Kivelson [9] gave the following expression for the linewidth contribution due to this mechanism

$$\alpha_{RS} = \frac{2}{\sqrt{3}} \frac{\hbar}{\beta_0 g} \frac{1}{12 \pi r^3} (\Delta g_{\parallel}^2 + 2 \Delta g_{\perp}^2) \frac{kT}{\eta} \quad (7)$$

where

$$\Delta g_{\parallel} = g_{\parallel} - 2.0023, \quad \Delta g_{\perp} = g_{\perp} - 2.0023.$$

Aqueous solution study of the complex gave four hyperfine lines corresponding to  $I = 3/2$  for copper. The individual hyperfine lines are neither completely

symmetric nor have equal intensity. The lines can be represented by the following equation :

$$\begin{aligned}\omega_0 &= g_0 \beta_0 H/\hbar + aM + \frac{1}{2} \hbar a^2 \times \\ &\quad \times [I + (I+1) - M^2]/g_0 \beta_0 H.\end{aligned}$$

The values of  $g_0$  and  $a$  obtained [26] are 2.129 and  $1.281 \times 10^9 \text{ s}^{-1}$  respectively.

The absolute sign of  $a$  was not determined. It was found that a positive value of  $a$  was quite convenient for calculations made here. Also the experimental linewidth parameter  $B$  comes out to be positive and the theoretical value of  $B$  can be positive only when  $a$  is positive. The experimental linewidth parameters  $A + A'$ ,  $B$ ,  $C$  and  $D$  have been obtained by solving simultaneously four equations like (6) each corresponding to one hyperfine linewidth. The experimental  $A'$  is obtained by subtracting the calculated value of  $A$  from the experimental  $(A + A')$ . The results in gauss are shown in table VI. The parameters have also been calculated theoretically with the help of equation (5) and are given in table VII.

Table VI. — Experimentally obtained linewidth parameters.

	$A + A'$	$A'$	$B$	$C$	$D$
Cu/L-Hydroxyproline	34.284	31.600	1.688	2.022	-0.272

Table VII. — (\*) *Calculated linewidth parameters,  $\tau_R$  and  $\alpha_{RS}$ .*

	<i>A</i>	<i>B</i>	<i>C</i>	<i>D</i>	$\tau_R$ ( $10^{-11}$ s)	$\alpha_{RS}$ (G)
Cu/L-Hydroxyproline	2.684	1.511	0.082	0.0025	0.752	67.127

(\*)  $T = 300$  K,  $\eta_{\text{water}} = 0.010$  02 poise.

The molecular hydrodynamical radius  $r$  was adjusted in such a way that it provides the best agreement between the experimental and calculated values of  $B$  and  $C$ . The data on experimental and calculated linewidths along with the  $r$  value are shown in table VIII. The linewidths for  $M = \pm 3/2$  lines are found to be larger than those from  $M = \pm 1/2$  lines.

Table VIII. — *Experimental and calculated linewidths along with hydrodynamical radius.*

	<i>M</i>	$\Delta H_e$ Gauss	$\Delta H_c$ Gauss	$\Delta H_e - \Delta H_c$ Gauss	<i>r</i> Å
Cu/L-Hydroxyproline	3/2	40.45	36.74	3.71	1.95
	1/2	35.60	35.06	0.54	
	- 1/2	33.98	33.55	0.43	
	- 3/2	37.22	32.19	5.03	

It is found from table VIII that the calculated linewidths differ from the experimental ones mainly in extreme lines. One reason may be that the parameters  $B$  and  $C$  are not of different signs. The linewidth contribution  $\alpha_{RS}$  because of spin-rotational relaxation mechanism is rather large as compared to residual linewidth  $A'$ . This might be so because the Hubbard theory [27], the basis of calculation of  $\alpha_{RS}$ , best applies to big molecules where strong intermolecular anisotropic interactions are present with the solvent molecules and as rotations are not relatively free [26]. Therefore it is quite likely that the above theory may not be holding well for the present molecule, Cu(II)-L-Hydroxyproline. Furthermore, the agreement between the theory and experiment is not so good as was found by Kivelson [26] in case of vanadyl acetylacetonate in chloroform. This is perhaps because the theory holds best for small values of  $|b/\omega_0|$  and  $|\Delta\gamma/\gamma|$ . In the present case the values of  $|b/\omega_0|$  and  $|\Delta\gamma/\gamma|$  are 0.03 and 0.10, respectively compared to 0.007 and 0.02 for vanadyl acetylacetonate. The values of  $|b/\omega_0|$  and  $|\Delta\gamma/\gamma|$  found here are similar to the values 0.01 and 0.10 obtained for copper acetylacetonate in chloroform [26].

3.3 MAGNETIC SUSCEPTIBILITY STUDY. — The apparatus for measuring magnetic susceptibility has been calibrated with the standard substances  $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$  and  $\text{Hg}[\text{Co}(\text{CNS})_4]$  having susceptibilities

$$5.85 \times 10^{-6} \quad \text{and} \quad 16.44 \times 10^{-6} \text{ cgs}$$

Table IX. — *The data on susceptibility and magnetic moment along with diamagnetic correction at room temperature (300 K).*

	Exptl. $\chi/g$ ( $10^{-6}$ cgs)	Diamagnetic correction $D/g$ ( $10^{-6}$ cgs)	$\chi_{\text{correct}}/g$ ( $10^{-6}$ cgs)	$\chi_{\text{theoret}}/g$ ( $10^{-6}$ cgs)	$\mu_e$ B.M.
Cu/L-Hydroxyproline	2.90	0.48	3.38	3.67	1.76

units respectively. The measured susceptibility was corrected for the diamagnetism of different diamagnetic atoms and groups present in the complex molecule [28]. Using this corrected susceptibility the experimental effective dipole moment,  $\mu_e$  has been determined [17, 28]. The theoretical susceptibility has also been estimated [17]. The data are shown in table IX.

Assuming a  $D_{4h}$  symmetry of the crystalline field and the energy level ordering as here, Bleaney *et al.* [29] and Owen [18] gave the following expressions for the magnetic moments along and normal to the tetragonal axis :

$$\begin{aligned} \mu_{\parallel}^2 &= 3 \left[ 1 - \frac{4 \lambda f_1^2}{\Delta_1} \right] + \left[ \frac{24 k T f_1^2}{\Delta_1} \right] \\ \mu_{\perp}^2 &= 3 \left[ 1 - \frac{\lambda f_2^2}{\Delta_2} \right] + \left[ \frac{6 k T f_2^2}{\Delta_2} \right] \end{aligned} \quad (8)$$

In above expression,

$$\begin{aligned} \Delta_1 &= \Delta E_{xy} - \Delta E_{x^2-y^2}, \quad \Delta_2 = \Delta E_{xz,yz} - \Delta E_{x^2-y^2} \\ f_1^2 &= \alpha^2 \beta_1^2, \quad f_2^2 = \alpha^2 \beta^2. \end{aligned}$$

For the determination of  $\mu_{\parallel}$  and  $\mu_{\perp}$ ;  $\alpha$ ,  $\beta$  and  $\beta_1$  have been taken from the glass study while  $\Delta_1$  and  $\Delta_2$  from optical absorption study of the complex. Average dipole moment  $\mu_e$  has been calculated from the relation

$$\mu_e^2 = \frac{\mu_{\parallel}^2 + 2 \mu_{\perp}^2}{3}.$$

The data thus obtained have been given in table X. The experimental dipole moment  $\mu_e$  has also been given for comparison purpose. From table X it is seen that there is a reasonable

agreement between the experimental and theoretically obtained  $\mu$  values which suggests that the assumed  $d_{x^2-y^2}$  ground state for the complex studied is appropriate.

Table X. — *The data of dipole moment using two methods, their difference and percentage change.*

	$\mu_{\parallel}$ B.M.	$\mu_{\perp}$ B.M.	$\mu_c$ B.M.	$\mu_e$ B.M.	$\mu_e - \mu_c$	$\pm$ % change
Cu/L-Hydroxyproline	1.96	1.86	1.89	1.76	- 0.13	7.4

**4. Conclusion.** — The optical absorption together with the magnetic susceptibility study concluded that the complex has the crystalline field of tetragonal symmetry and the ground state is  $d_{x^2-y^2}$ . The ESR study in polycrystalline phase showed that the line-shape is Lorentzian and an increase in linewidth of the complex as compared to the pure copper salt is due to a greater reduction in exchange than that of dipolar interaction on complexation. The glass along with the optical absorption study indicates that there exists a definite bonding between the metal ion and the ligands and that both the bondings, namely in-plane and out-of-plane, are fairly covalent. From the linewidth study in solution it is inferred that a better fit of theoretical data with the experimental one can be found by taking into account the contributions of significant mechanisms such as spin-rotational relaxation or so. The results obtained for the effective magnetic moment from two methods, first, using

measured susceptibility and second, with the help of optical absorption and glass phase ESR study of the complex, are in a reasonable agreement indicating thereby that both the macroscopic and microscopic methods are equally valid for such systems. Thus all the studies undertaken here are complementary to each other and are useful to reveal the information regarding the physical-chemical nature of the complex and the magnetic as well as non-magnetic interactions present between the metal ion and the ligands.

**Acknowledgments.** — The authors are thankful to the Directors, NPL, New Delhi, IIT, Kanpur and CDRI, Lucknow for providing the necessary facilities to complete the work presented here. The help extended by Dr. G. D. Sootha and Dr. S. K. Gupta of NPL is also acknowledged. One of us (RK) is thankful to UGC and CSIR, New Delhi for financial assistance.

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