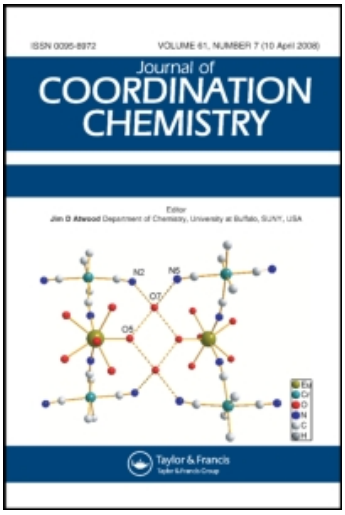

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SERINE, THREONINE AND α-HYDROXYAMINE COORDINATION TO CUPRIC IONS BY HYDROXYL-OXYGEN-METAL BONDS

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SERINE, THREONINE AND α-HYDROXYAMINE COORDINATION TO CUPRIC IONS BY HYDROXYL–OXYGEN–METAL BONDS

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The copper complexes of serine and threonine have been studied under a wide pH range. Results obtained by conductivity measurements, potentiometry, visible and EPR spectroscopy all indicate that hydroxyamino acids are coordinated in a tridentate fashion. Evidence is presented which shows that metal-alkoxy bonds are formed in basic solutions and that the deprotonated ligands then form anionic copper complexes.

INTRODUCTION

α-hydroxyamino acids are interesting ligands that give stable metal complexes. Of the three functional groups in serine and threonine, involvement of the amino and carboxylato functions in chelate formation is well recognized. However, coordination to Cu^{++} ions by the hydroxyl groups is difficult to establish. The crystal structure determinations of $Cu(serine)_2$ and $Cu(l\text{-thréonine})_2$ have not revealed any metal-hydroxyl interactions,[1,2] but these and other amino acid complexes exist in several geometric and stereoisomeric forms.[3–6]

The aqueous solution chemistry of hydroxyamines has been thoroughly investigated[7,8] and evidence has been found pointing to increased stability of hydroxyamine complexes compared to similar amine complexes. Under basic conditions, titration of "extra" protons has been reported ocassionally[8–11] but it remains impossible, by potentiometric measurements alone, to determine the origin of these protons. Coordinated water molecules or alcohol groups or both could be deprotonated to give hydroxy or alkoxy-metal bonds.

We have reported previously our EPR investigations of the Cu^{++} complexes of vitamin B6 with dopamine and octopamine[12] and have found that the presence of a hydroxyl group α to the amine notably influences the chemistry of these systems. Due to difficulties in characterizing hydroxyamine complexes which also contain catechol groups, and because simpler aliphatic hydroxyamines and hydroxyaminoacids also contain the amino-ethanol moiety common to adrenaline and other biologically important molecules, we now wish to report the results of our investigations of the coordinating behaviour of the title ligands, by potentiometry, conductimetry, EPR and visible spectroscopy.

EXPERIMENTAL

Conductivities were measured with a CD6N conductivity bridge by SOLEA and a CMO5 Tacussel electrode (France). The cell constant was calculated using 0.1 M KCl. Visible spectra were recorded on a Cary 14 spectrophotometer for the solution spectra and on a Unican SP. 800 for the reflectance spectra. Potentiometric titrations were carried out by standard procedures using a constant 0.10 M KNO_3 ionic strength.[13] Stability constants were refined using the SCOGS program.[14] An E-9 Varian EPR spectrometer was used with a flat quartz aqueous cell assembly for the solution spectra. Quartz tubes of 2 mm bore and 3 mm width were used for the solid state and frozen solution spectra.[15]

RESULTS

The visible spectra of solutions of copper hydroxy-amino acid complexes are shown in Figure 1. An extra band appears as a shoulder in basic solutions near 520 nm. The conductivity measurements show that the copper amino acid complexes are undissociated or neutral molecules in the pH range 6 to 9, but that under basic conditions ionic species are formed. Figure 2 shows the corrected conductivities as a function of the added base, and reveals breaks in the graph for stoichiometric ratios of Cu^{++}:OH^-. The potentiometric results are close to previous observations made at similar ionic strengths and temperatures (25°C) and are summarized in Table I.

Solutions of bisglycinatocopper(II) do not show ligand hyperfine structure, even under basic conditions. However, both serine and threonine give resolved nitrogen hyperfine splittings on the high-field copper absorption line at pH > 10. Copper chloride propanolamine solutions give strongly temperature and pH dependent spectra, with nitrogen hyperfine interactions resolved at lower temperatures (Figure 3).

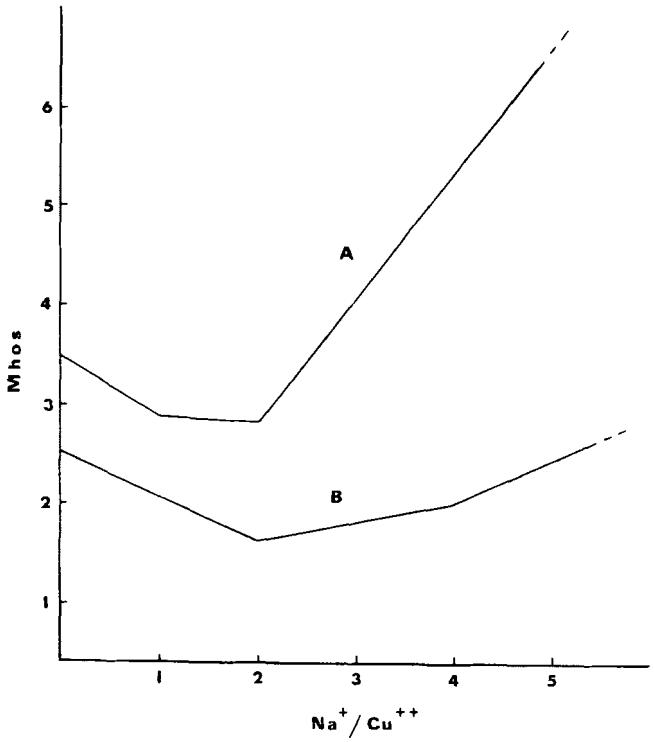


FIGURE 2 Variation in conductances of copper glycinate (A) and copper serinate (B) as a function of the molar ratio of base to metal. Conditions: 0.2 mmoles Cu + 0.4 mmoles amino acid in 50 ml H_2O.

DISCUSSION

Bisglycinatocopper (II) has a low equivalent conductivity, $\Lambda_0 = 46\ \Omega^{-1}\ cm^{-1}$,[16] typical of

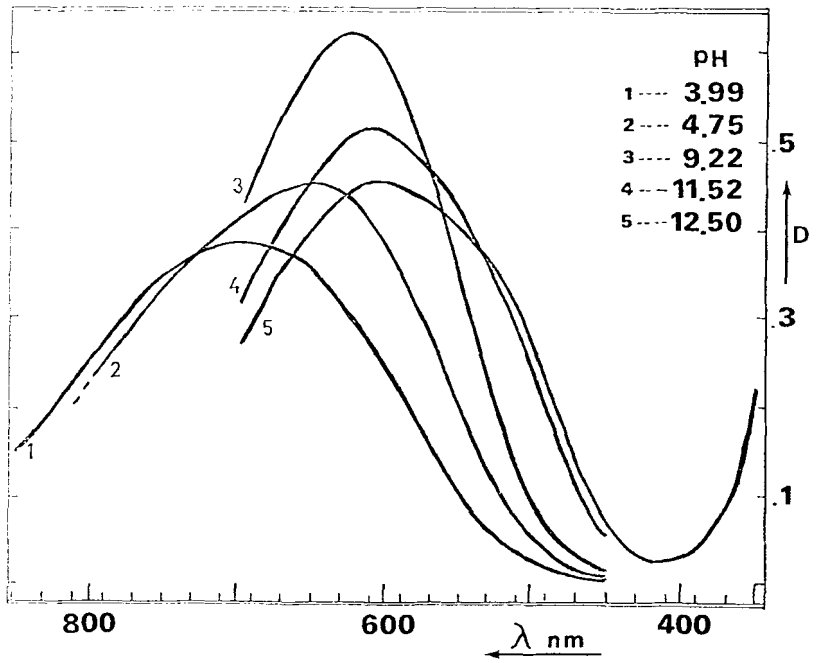


FIGURE 1 Visible absorption spectra for solutions of copper DL serine)$_2$ as a function of pH.

TABLE I
Stability constants for the copper–serine system.

Ref.	log K_1	log K_2	log β_2	log K_3	log β_3	log K_4	log β_4	Conditions
22	7.56	6.45	14.01					I = 0.16
24	7.65	5.85	13.50					I = 0.05
25	7.656	6.356	14.012					I = 0.15 (KNO_3)
26	7.85	6.65	14.50					I = 0.16 M KNO_3
6	7.858	6.57	14.428					I = 0.1 M KNO_3
27	7.89	6.51	14.40					I = 0.2 M KNO_3
28	7.92	6.65	14.57					I = 0.1 M KNO_3
29	7.93	6.55	14.48					I = 0.05 (KCl)
30	8.95	7.28	16.23					I = 3 M $KClO_4$
31	8.01	6.574	14.584	−9.812	4.772	−10.952	−6.18	I = 0.15 M NaCl
10	7.95	6.73	14.68	−10.25	4.43	−11.26	−6.83	I = 1 M $NaClO_4$
9	—	—	—	−10.03	—	−10.95	—	I = 1 M KNO_3
32	7.92	6.81	14.73	−10.35	4.37	−11.14	−6.77	I = 0.1 M KNO_3

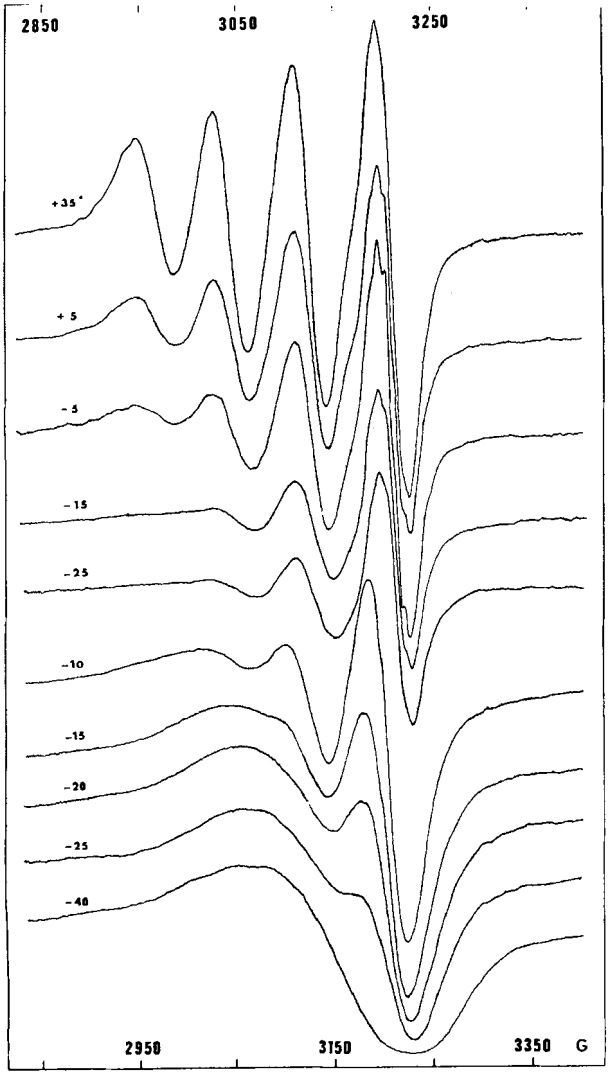


FIGURE 3 Temperature dependence of copper propanolamine complex solution epr spectra at pH 9.69. Top five spectra taken as T decreases, bottom five, at T increases.

undissociated copper amino acid complexes. Figure 2 shows how the conductivity of a copper nitrate solution containing a stoichiometric quantity of amino acid varies as a function of added base. The conductivities decrease as complex formation proceeds. Breaks in the curves are obtained for stoichiometric amounts of added base, because the conductivities have been corrected for the conductivity of Na^+ (according to the volume of NaOH added), and the conductivity of OH^- (according to the measured pH of the solution). Otherwise, only smooth decreases in resistivity are observed. The breaks are seen when one and two moles of base are added to copper-glycine solutions, corresponding to the formation of 1:1 and 2:1 complexes with different molar conductivities. Thereupon, the pH rises sharply from 8 to 10.5, as do the magnitudes of the conductivity corrections. It has been assumed that the contribution of NO_3^- ions to the total conductivity varies linearly with dilution and does not affect the main features of the plots.

In the case of copper-serine solutions, in addition to the discontinuity after formation of the 2:1 complex, another break appears when 4 moles of base have been added per mole of copper. It should be noted that after the initial decrease in conductivity corresponding to the formation of the bis-chelate complexes, the conductivity increases as would be expected for deprotonated complexes. Nevertheless, formation of an anionic complex is not proven, since the change in conductivity could also be due to changes in the size, conformation or mobility of the complexes.

More reliable results are obtained when pure copper-amino acid complexes are dissolved for conductivity measurements. Thus the initial pH is nearly neutral, and the ionic force low. Adding base to bisglycinatocopper(II) then results in a slow decrease of the corrected equivalent conductivity, perhaps related to a decrease in dissociation as the pH rises. Bisserinatocopper(II) has an appreciably lower

conductivity than bisglycinatocopper(II), showing it must be even less dissociated in aqueous solution. As base is added, the conductivity rises, favoring the hypothesis of anionic complex formation, and reaches a maximum near the stoichiometric Na^+:Cu^{++} ratio of 2:1.

The solid state reflectance spectra of bisglycinatocopper(II) and bisserinatocopper(II) show very broad absorption bands. As in the solution spectra in Figure 1, the wavelength of maximum absorption is higher for the glycine complex (λ_{max} = 645 nm) than for serine complex (λ_{max} = 600 nm). These λ_{max} values are typical of amino acid complexes of copper with two nitrogens and two oxygens coordinated to the metal in a square planar geometry.[17] The color of the hydroxyamino acid complexes changes from blue to violet as the pH becomes basic and similar violet colors are observed for aminoethanol complexes.[18,19] Extinction coefficients vary from 31 to 52 to 59. The shift of the absorption towards lower wavelengths for copper hydroxyamino acid complexes is not observed for bisglycinato- or bisalanitocopper(II) can be explained according to several theories.

For copper glycinate, the absorption envelope results from the two $^2Eg \leftarrow {}^2A_1g$ and $^2Eg \leftarrow {}^2B_1g$ transitions.[20] Lowering the symmetry (e.g. from O_h to D_{2h} or C_{2v}) can raise the state energy level by splitting the ^2Eg state.[21] A similar effect can be attributed to pentacoordination.[22] The simplest explanation is to consider the crystal field splitting as larger in copper hydroxyamino-acid complexes than in bisglycinatocopper(II). If the α hydroxyamino acids are considered as tridentate, then it seems logical they could impart a stronger crystal field strength. Furthermore, under basic conditions, if the "soft" hydroxyl group is changed into the "hard" alkoxy group, the bathochromic shifts due to these ligands can also be explained.

The formation constants gathered in Table 1 can be divided into two types. The majority of authors[23-30] reported stability constants for 1:1 and 2:1 complexes only, even when they knew of the possible existence of deprotonated species.[6] Kruck and Sarkar,[31] Ptak and coworkers,[10] and Janjic[9] listed constants for the "autoprotolysis" of copper-serine complexes. Our results largely confirm the values obtained by these authors, and indicate it is worthwhile, in hydroxyamino acid complexes to investigate the highly basic pH range (10 to 12) in order to more fully characterize these systems.

Braibanti[33,34] found deprotonated copper complexes and dimeric alkoxy-bridged species with aminohydroxy acids and concluded they were different, for some unknown reason, from copper serine and threonine complexes. But our results show that serine is not an exception, and that most hydroxyamino acid systems do tend to form deprotonated species. Loss of protons corresponds to acid dissociation constants and that is why log K_3 and log K_4, in Table I, are negative. The equilibria considered can be formulated as in Eqs. (1) to (4) where A represents an amino acid.

$$Cu^{++} + A^- \rightleftharpoons CuA^+ \quad (1)$$

$$CuA^+ + A^- \rightleftharpoons CuA_2 \quad (2)$$

$$CuA_2 \rightleftharpoons Cu(H_{-1}A)A^- + H^+ \quad (3)$$

$$Cu(H_{-1}A)A^- \rightleftharpoons Cu(H_{-1}A)_2^{2-} + H^+ \quad (4)$$

The corresponding equilibrium constants are expressed as concentration constants:

$$K_1 = \frac{[CuA^+]}{[Cu^{++}][A^-]} \qquad K_2 = \frac{[CuA_2]}{[CuA^+][A^-]}$$

$$K_3 = \frac{[Cu(H_{-1}A)A^{-1}[H^+]}{[CuA_2]}$$

$$K_4 = \frac{[Cu(H_{-1}A)_2^{2-}][H^+]}{[Cu(H_{-1}A)A]}$$

$$\beta_2 = \frac{[CuA_2]}{[Cu^{++}][A^-]^2} \qquad \beta_3 = \frac{[Cu(H_{-1}A)A][H^+]}{[Cu^{++}][A^-]^2}$$

$$\beta_4 = \frac{[Cu(H_{-1}A)_2^{2-}][H^+]^2}{[Cu^{++}][A^-]^2}$$

However, from a numerical point of view, Eqs. (5) and (6) are identical to Eqs. (3) and (4) where it is assumed that water

$$CuA_2 + H_2O \rightleftharpoons Cu(OH)A_2^- + H^+ \quad (5)$$

$$Cu(OH)A_2^- + H_2O \rightleftharpoons Cu(OH)_2A_2^{2-} + H^+ \quad (6)$$

molecules are deprotonated to yield hydroxyanions coordinated to copper. Such complexes have been proposed previously[35,36] on the basis of calorimetric work.

The enthalpies of formation for copper serine and threonine complexes change from ≈ -13 Kcal mole^{-1} to over -23 Kcal mole^{-1} as the pH is raised above pH 10. Accordingly, the formation of poly-nuclear hydroxy complexes has been assumed in basic conditions. However, it remains difficult to explain why bisglycinatocopper(II) does not yield similar hydroxo species. Enthalpies of formation obtained calorimetrically and by the log K temperature coefficient method agree well.[29] This indicates that the normal 1:1 and 2:1 chelates are formed in a pH range independent of the deprotonation range. This is seen

clearly in Figure 4, where the distribution of species is plotted as a function of pH.

The enthalpies of formation of serine and threonine copper complexes are nearly one Kcal mole^{-1} more exothermic than the corresponding enthalpies of formation of alanine and α amino-butyric acid complexes. Also, on the basis of the differences pKa-log K_n, the stabilities of the hydroxyamino acid complexes are greater than those of the corresponding "regular" aminoacids. Yet, the inductive effect of the hydroxyl groups would be to weaken the metal-nitrogen bonds. Therefore, the comparatively large stabilities of copper hydroxyamino acid complexes must be due to the formation of copper-hydroxyl group bonds in addition to copper-amino and carboxylato group bonds.

Similar comparisons between acetic acid and glycolic acid complexes lead to the conclusion that metal hydroxy-oxygen bonding is likely.[37] It has been argued that if the hydroxyl groups are to be coordinated in serine and threonine complexes, the resulting structures would impose considerable steric strain,[6] and on this basis, an outer-sphere coordination of the hydroxyl groups, with hydrogen bonding to inner-sphere coordinated water molecules has been proposed. This assumed that the staggered conformation with the OH group *gauche* to both CO_2^- and NH_2 groups was unfavorable, but on the contrary, n.m.r. studies have shown that hydroxyamino acids exist predominantly in this conformation, due to intramolecular hydrogen bond formation. The most reasonable way to explain the array of data is therefore to assign flexible structures to the ligands, which will allow the three functional groups to enter the metal coordination sphere under basic conditions. The epr spectra observed for the studied compounds further support such structures. Indeed, there is a difference in the solution spectra of copper amino acid and copper hydroxyamino-acid complexes. Whereas bisglycinatocopper(II) has a pH independent spectrum, bisserinatocopper(II) shows two distinct absorptions corresponding to two different complexes. Near neutral conditions bisserinatocopper(II) $g_0 = 2.130$ and $A_0 \approx 70$G while under basic conditions $g_0 = 2.119$ and $A_0 \approx 87$G. Similarly for bisthreoninatocopper(II), g_0 changes from 2.12_8 to 2.11_6 and A_0 from 72G to 84G when the pH becomes basic.

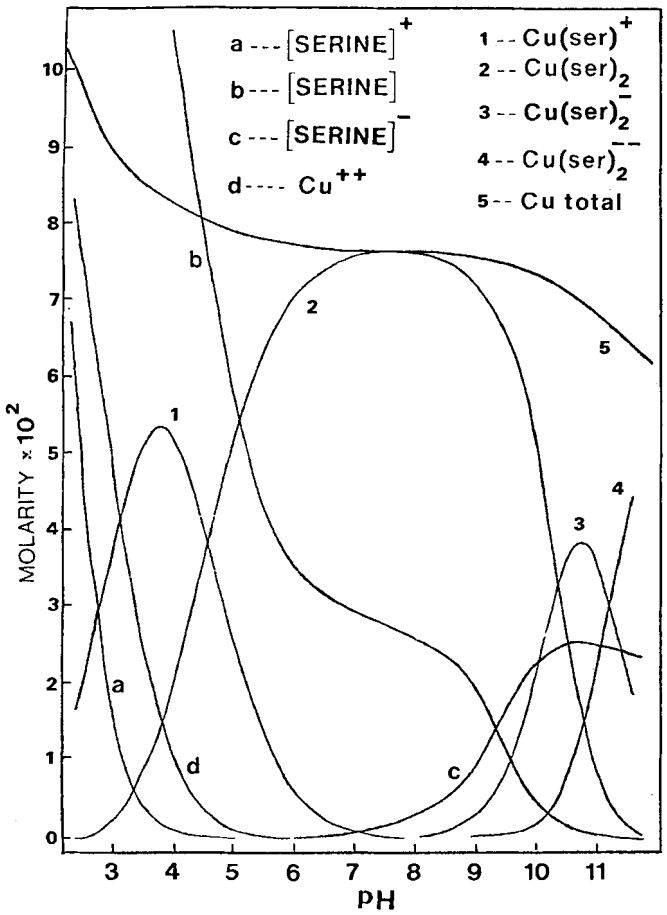


FIGURE 4 Distribution of species of the copper DL serine system, as a function of pH.

Hyperfine splitting which can be attributed to nitrogen ligand nuclei appears on the copper serinate spectrum with $A_N \approx 9$G. This hyperfine splitting is better resolved for the bisthreoninatocopper(II) system, where $A_N = 9$G and the five line pattern can be attributed to coupling with two equivalent nitrogens. According to Gersman and Swalen[38] resolution of ligand hyperfine structure depends, at least qualitatively, on the stability of the complexes. It has been proposed that ligand relaxation by fast chemical exchange can contribute to the loss of resolution of hyperfine splittings. This agrees well with the general failure to detect nitrogen hyperfine in copper amino acid complexes.[39] On this basis, coordinated serine and threonine must be exchanging more slowly than other amino acids bound to copper, as expected for tridentate *vs* bidentate ligands. We also observed that for 0.005 M Cu^{++} solutions, nitrogen hyperfine structure begins to fade when the hydroxyamino acid concentration increases from 0.04 M to 0.08 M. This is probably due to a faster second-order exchange rate at high ligand concentrations. This favors our interpretation of ligand hyperfine resolution as being due to slowly exchanging tridentate ligands and not to a different hybridization of the nitrogen atom or to an unusual coordination geometry.

Frozen solution spectra also reveal similar trends in A and g values.[40,41] Nieman and Kivelson's theory[42] predicts larger copper hyperfine constants and smaller $g_{\parallel}$ and $g_{\perp}$ values when the metal-ligand bonds becomes more covalent. This is exactly what is observed in the deprotonated species, indicating the ligands are more tightly bound.[43] As for the solid state spectra, only the copper serine complexes obtained from neutral aqueous or ethanolic solutions were examined, as basic solutions failed to yield pure compounds. The spectra resemble previous observations.[44] It is interesting to note that the $Cu(L\text{-}ser)_2$ complex gives a more symmetrical adsorption than the $Cu(DL\text{-}ser)_2$ complex. The situation here is probably analogous to the $Cu(L\text{-}met)_2$ and $Cu(DL\text{-}met)_2$ complexes[45] where it has been shown with K-band spectra the main difference is simply due to wider $Cu(L\text{-}met)_2$ adsorptions.

As for the copper propanolamine solutions, potentiometric titrations were unsuccessful at near stoichiometric metal-ligand proportions due to copper hydroxide formation, as observed previously.[46] Organic solvents[47] or basic solutions help, though as noted by Bjerrum and Refn,[48] ethanolamine tends to form complexes of the alkoxo anion at higher pH, but it is difficult to distinguish this effect from formation of mixed hydroxo species.

Epr spectroscopy provides a means of examining the changes in the nature of the complexes formed with propanolamine. As shown in Figure 3, a pronounced asymmetry arises in the four line copper hyperfine structure. This asymmetry increases as the temperature is lowered, or as the ligand concentration (and viscosity) increases. These observations agree with McConnell's theory,[49] which shows how the hyperfine linewidth depends on the nuclear magnetic quantum number. Nitrogen hyperfine splitting of 10G can be observed at intermediate temperatures, indicating that the loss of hyperfine interaction at higher temperatures can be attributed to rapid ligand exchange, as has been discussed for the amino acid cases. Conversion of the epr absorptions to more symmetrical curves is due to faster rotational motions of the complex ions at higher temperatures.

The pH dependence of the epr spectra gives some insight on the distribution of species (see Figure 5). The broad absorption observed in acidic media (pH 3.75) is typical of the rapidly tumbling and exchanging $Cu(H_2O)_6^{++}$ cation. At higher pH, the solutions turn darker blue, as do copper-amine solutions, and this results in a narrower line, with a g-value of 2.13, in agreement with copper amine complex formation. Simultaneously, a four line pattern emerges, typical of copper chelate complexes. It can be postulated that

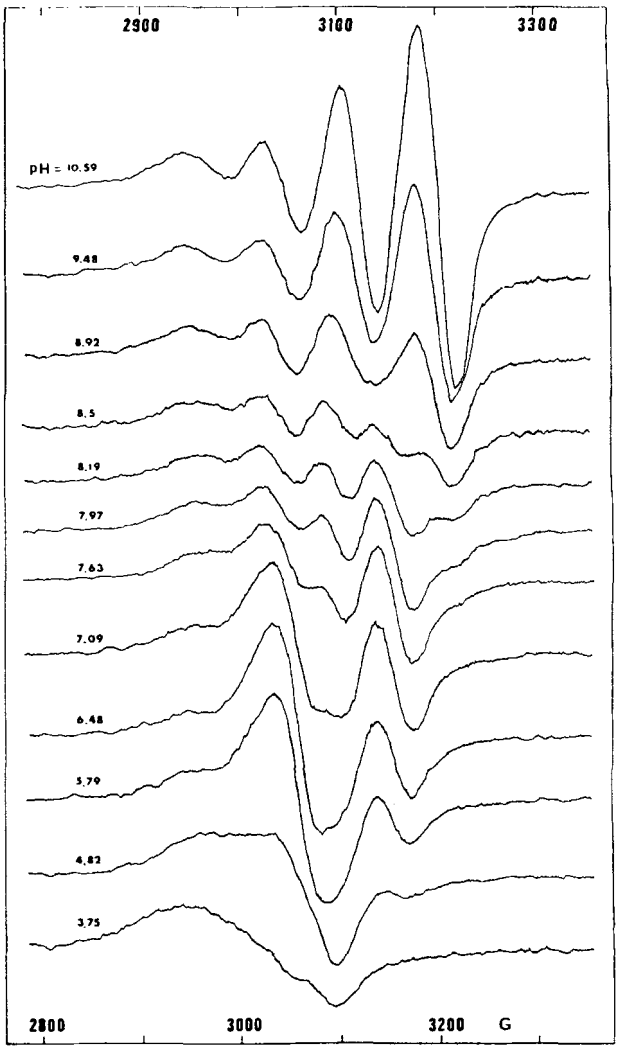


FIGURE 5 pH dependence of the room temperature epr spectra of copper propanolamine complexes, pH indicated.

propanolamine forms a square planar copper chelate, involving NH_2 and OH coordination, as the predominant species between pH 7.5 and pH 8.2. As the pH increases, this species is replaced by a new one with clearly different spectral parameters: g_0 decreases from 2.127 to 2.115 and A_0 increases from 55G to 75G. These changes are similar to the ones observed for hydroxy-amino acid complexes and are satisfactorily explained by stronger metal ligand bonds. This is also confirmed by frozen solution spectra which show $A_{\parallel}$ = 180G and $g_{\parallel}$ = 2.232 for both the neutral and basic solutions of copper propanolamine. In these spectra, only the $g_{\perp}$ part of the absorption changes with pH, showing that coordination in the axial position is

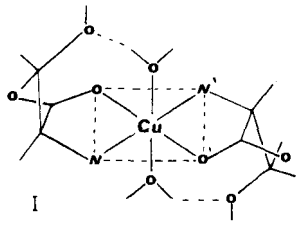
TABLE II
Epr parameters for the copper complexes of threonine, serine and propanolamine.

Complex	pH	g_0	A_0	A_N	$g_\parallel$	$A_\parallel$
Serine	8.5	2.130	70	—		
	11.9	2.119	87	9	2.229	180
Threonine	9.4	2.128	72	—	2.245	183
	12.5	2.116	84	9	2.221	197
Propanolamine	3.75	2.157	—	—	—	—
	6.48	2.131	—	—	2.242	152
	8.19	2.127	55	—	2.230	180
	10.59	2.115	75	10	2.232	180

$g_\parallel$ and $A_\parallel$ values for serine complexes quoted from Ref. 41.
$g_\parallel$ and $A_\parallel$ values for threonine complexes quoted from Ref. 43.

not a determining factor. The data is consigned in Table II.

In conclusion, formation of hydroxo species seems less likely than simple conversion of amino-alcohol chelates to amino-alkoxy chelates. Mechanistically, formation of the complexes can be viewed as shown in Figure 6. At neutral pH, copper hydroxyamino acid complexes adopt structure I, with the hydroxyl group strongly hydrogen bonded to the axially coordinated water molecules. As the pH increases and the hydroxyl group becomes deprotonated, it enters the copper coordination sphere giving structure II. Finally, the amino and alkoxo groups form the main coordination bonds to copper (square plane indicated by full line) and the carboxylates occupy the labile axial sites. Formation of the anionic complex then accompanies inversion of the axial axis undergoing dynamic John-Teller distortions.



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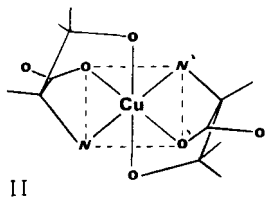

II

FIGURE 6 Solution structures proposed for copper hydroxyamino acid complexes I and the anionic species II. In copper amino acid complexes, the normal bond lengths are Cu–N ≈ Cu–O 1.96 Å. Thus, N–O ≈ 2.56 Å, O–N′ ≈ 2.88 Å, N–Cu–O ≈ 86° and O–Cu–N′ ≈ 94°. For the tridentate amino acid, with the same Cu–N and Cu–O distances, and with axial O at 2 Å, the alpha C lies 0.88 Å above the square plane (dotted lines). Then, N–O ≈ 2.80 Å, O–N′ ≈ 2.56 Å, N–Cu–O ≈ 96° and O–Cu–N′ ≈ 84°. There is no apparent strain in the structure.

ACKNOWLEDGEMENTS

We thank one referee who not only emphasized that the carboxylate groups were in axial coordination positions under basic conditions, but also pointed out the visible absorption spectra agreed well with a penta-coordinated structure for $[Cu(H_{-1}A)_2]^{2-}$ with one non-coordinated carboxylate anion. A recent review has appeared on complexes of α-amino acids with chelatable side chain donor atoms.[50] This work was funded in part by the Conseil de Recherche en Sciences Naturelles et en Génie.

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