TABLE I. Visible and ESR Spectral Data for 1:1 Reduced Glutathione–Cu(II) Complexes at Various pH.

Species	(pH)	λ_{max} (nm)	ϵ/Cu^{2+}	$g_\parallel$	$g_\perp$	$A_\parallel$ (G)	$A_\perp$ (G)
I, blue	(8.0)	620	60	2.256	2.055	163	–
II, green	(9.5)	615	70	2.258	2.059	165	–
III, violet	(11.3)	593	95	2.251	$g_x = 2.047$ $g_y = 2.038$	177	$A_x = 43.8$ $A_y = 36.0$
IV, $[Cu(OH)_4]^{2-}$	(12.5)	593	105	2.239	2.045	186	30.0

nitrogen, the glycinyl terminal carboxylate oxygen and the two protonated amide in an approximate planar coordination while the cystinyl sulfur is bonded apically to form a square-pyramidal. ESR parameters and absorption maximum are shown in Table I.

On the other hand, for the 1:1 and 1:2 oxidized glutathione and Cu(II) systems, our results are in agreement with those reported by White *et al.* [2] and Kroneck [3], respectively.

Since the discovery of superoxide dismutase (SOD) in 1969, there has been a search for low molecular weight complexes with high SOD activity. We examined the ability of I to act as a superoxide dismutating agent. The blue complex I at pH 7.8 inhibits the reduction of cytochrome c by the xanthine–xanthine oxidase system. The second rate constant of the reduction with O_2^- was estimated to be 2×10^7 M^{-1} sec $^{-1}$ which is close to the value (5×10^7 M^{-1} sec^{-1}) of the antiarthric drug, salicylate–Cu(II) complex. The Cu(II) chelate of glutathione is able to act as a stronger superoxide dismutating agent than the ligand (6.7×10^5 M^{-1} sec^{-1}). A role of complex I as a scavenger of O_2^- is suggested in biological systems.

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Solid and Ethanolic Solution State Behavior of N-Tosylglycinate–Copper(II) System

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In the copper(II) ion–N-tosylglycinate system, in both the solid state and in aqueous solution, it was suggested that the ligand presents the properties of both L-α-amino acids [1] and their N-acetyl or N-benzoyl-derivatives [2] depending on the pH of the media [3]. In this paper we report an investigation on the same system in ethanolic solution in order to compare the coordination behavior of this amino acid with those of N-acetyl and N-benzoyl-amino acids also in this media.

From ethanolic solution two compounds of formula $[Cu(TsglyH)_2]_n$ (green) and $Na_2[Cu(Tsgly)_2]$ (blue) (TsglyH and Tsgly = N-tosylglycinate monoanion and dianion, respectively) were isolated. In the latter complex, which is similar to a compound previously separated from aqueous solution, the ligand acts as bidentate through the carboxylate oxygen atom and the deprotonated sulphonic nitrogen atom. For the green compound the crystal structure was also determined. Crystals are monoclinic, space group $P2_1/n$, with $Z = 4$ in a unit cell of dimensions: $a = 24.655(3)$, $b = 7.697(2)$, $c = 12.378(3)$ Å, and $\beta = 87.34(8)°$, and $R = 0.052$. The structure (Fig. 1) is built up of one dimensional polymeric chains of binuclear units, showing the cupric acetate

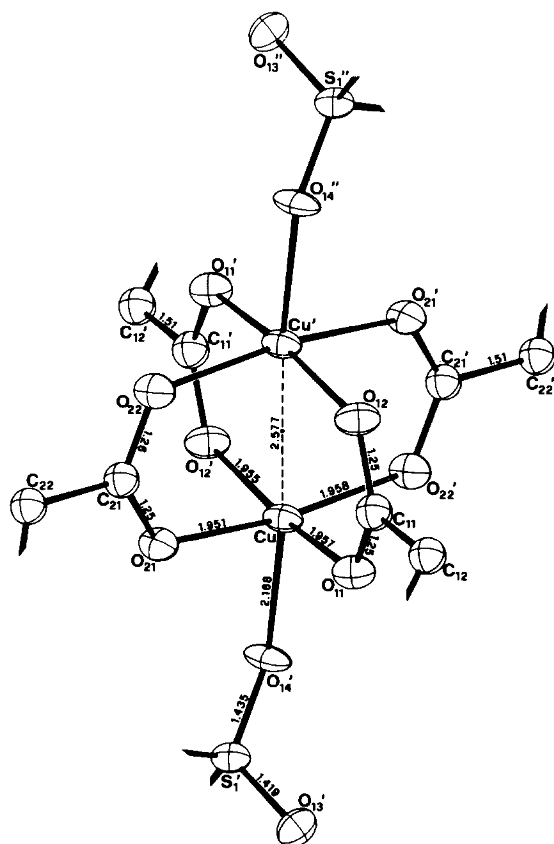

Fig. 1. Structure of $[Cu(TsglyH)_2]_n$.

structure, linked *via* Cu–O (sulphonic) bonds. Its magnetic and spectroscopic properties are interpreted on the basis of the crystal structure. The exchange integral (–2J) is 353 ± 4 cm^{-1}.

In ethanolic solution at metal ion concentrations similar to those normally found in biological systems, by polarographic measurements, for $C_{NaOH}/C_{Complex}$ ratios between 1 and 3 the $Cu(TsglyH)_2$ species is the only present, while for ratios greater than 4 the $Cu(Tsgly)_2^{2-}$ prevails.

The main conclusions from this work are:

In ethanolic media the N-tosylglycine parallels the behavior in aqueous solution, even if more complicated equilibria are present in this last solvent. The separation of only two solid compounds from ethanol with respect to the four from aqueous solution also confirm this.

These results, and those previously observed for the N-acetyl and N-benzoyl-amino acids [2], suggest as a general rule that the ethanolic media enhances the behavior as simple carboxylate ligands of these amino acids, favouring the separation of compounds which possess dimeric arrangement of the copper(II) acetate type with strong antiferromagnetic exchange.

Nevertheless, in the N-tosylglycinate–copper(II) ion system in ethanolic solution in the experimental conditions (*i.e.* at metal ion concentrations close to those of biological systems), there is no evidence for a binuclear species.

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The Use of Metal Additive in Reversed Phase Liquid Chromatography: Structure–Retention Relationships

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The fact that biologically active molecules such as amino acids, nucleotides, nucleosides and their bases form complexes with metal cations is well known. A great deal of work is devoted to the elucidation of properties and structures of such complexes. To date most of the research in the field was done using spectroscopic and electrochemical methods. We wish to report here the use of liquid chromatography for investigating the properties of such complexes. The experimental system is rather simple, consisting of a reversed phase column and an aqueous mobile phase. The mobile phase contains the metal cations under study. To such a system we inject amino acids, nucleotides, nucleosides and their bases.

These solutes form complexes with the cations in the mobile phase. Since the nature of the complexes is different from that of the parent compounds, their chromatographic behavior changes. The change can be related to the properties and structures of the complexes.

The partition coefficients, and hence retention times, of all amino acids studied increased when the metal cations were introduced to the mobile phase. The increase in the retention is related to the stability of the complex. For example the retention time order is $t_R(Cu) > t_R(Ni) > t_R(Zn) > t_R(Co)$, where $t_R(M)$ indicates the retention time with metal cation M in the mobile phase. The magnitude of the amino acids–metal complex formation constant is $K_f(Cu) > K_f(Ni) > K_f(Zn) > K_f(Co)$. Since the chromatographic system is that of reversed phase, longer retention times can indicate greater hydrophobic interactions. In the present case the greater hydrophobicity is due to partial charge neutralization of the amino acid by the metal cations. The degree of neutralization is a function of the stability of the complex.