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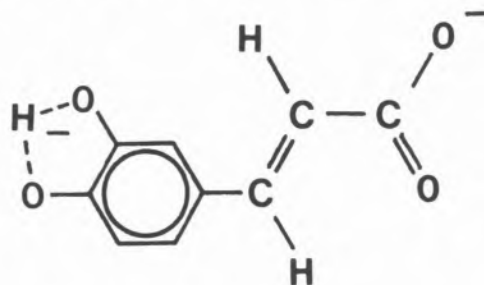
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COMPLEXATION OF COPPER(II) IONS BY CAFFEIC ACID

The bioavailability to plants of metal ions, either as micro-nutrients or as toxins, is strongly influenced by coordinating ligands which may be present in the soil or the artificial nutrient solution in which the plant grows [1]. In order to contribute to the understanding of the role of coordination equilibria in the transport of metal ions to plant roots, we are undertaking chemical speciation studies of soil and nutrient solutions by means of computer simulation [2,3]. Amongst the information needed for our computer models are formation constants for the manifold metal-ligand-proton complexes that can be found. Of special interest are various phenolic ligands which are known to be exuded by plant roots under certain conditions and which are believed to participate in the transport of iron from the surrounding soil or nutrient solution to the root membrane [4]. The root-exuded phenolic compound of major importance is caffeic acid. Indeed, it has been postulated that under the conditions prevailing in soils, caffeic acid tends to reduce iron (III) to iron (II), the necessary state of oxidation for iron ions to be absorbed by plant roots [4]. Since caffeic acid can potentially form complexes with all the types of metal ion which occur in soil and nutrient solutions, it is an essential component for inclusion in our speciation models. Moreover, since there is a paucity of formation constant data reported in the literature for caffeate-metal-proton complexes, we are undertaking an extensive programme of investigation into the solution equilibria of these systems. On our poster, we intend to present re-

sults obtained by glass electrode potentiometry and NMR for copper (II).

In its own right, caffeic acid is an interesting coordinating ligand purely from the inorganic chemical point of view. This arises from the two coordination sites, one at each end of the molecule. Taking the ligand species to be the dianion,



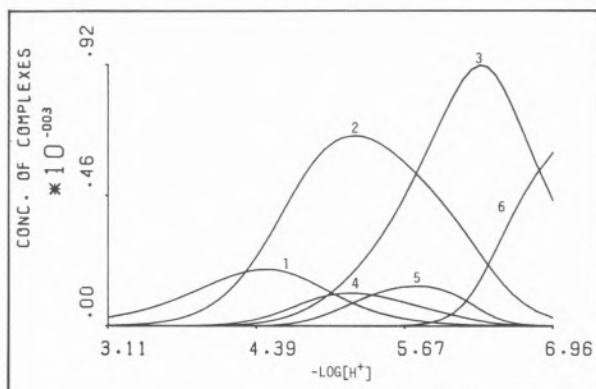
(denoted hereafter by L^{2-}) protonation constants have been determined, yielding the results in the Table. Note that whereas one of the catecholic oxygens is reasonably acidic, with a pK_a of 8.72, the second is very strongly basic (cf. catechol: $pK_{a1} = 13.0$, $pK_{a2} = 9.23$) [6]. This has been attributed to hydrogen bonding between the hydroxyl and phenoxide groups [7]. We have made no attempt to determine the first protonation constant of the trianion of caffeic acid.

Table
Logarithms of protonation constants (β_H) determined for L^{2-} at 25°C and $I = 0.100 \text{ mol dm}^{-3}$ (Na) [Cl]. d = the standard deviation in $\log \beta_H$. n = the number of experimental observations

Reaction	$\log \beta_H$	d	n
$L^{2-} + H^+ \rightleftharpoons LH^-$	8.72	.003	389
$L^{2-} + 2H^+ \rightleftharpoons LH_2$	13.13	.004	389

Preliminary results obtained for the complexation titrations have been used to construct the diagram in the Figure. The latter shows the distribution of caffeate-copper(II)-proton complexes detected in aqueous solutions with total concentrations of the components that are typical of the titrations in this study.

Although we can be reasonably certain of the stoichiometry of the species in the figure, the structures are not known at this stage and may be merely speculated upon. Thus the following are suggested



Figure

Concentrations of complexes present as a function of pH for the caffeic acid-copper (II) system when the total concentrations in mmol dm^{-3} of L^{2-} and Cu^{2+} are 8.6 and 2.0, respectively. Temperature = 25°C and $I = 0.100 \text{ mol dm}^{-3}$ (Na) [Cl]. Species: (1) LCuH^+ ; (2) LCu ; (3) $(\text{LH}_{-1})\text{Cu}$; (4) $(\text{LH}_{-1})\text{Cu}_2$; (5) $(\text{LH}_{-1})_2\text{Cu}_3$; (6) $(\text{LH}_{-1})_3\text{Cu}_2$

as being plausible. (1) LCuH^+ : copper coordinated to the carboxylate; (2) LCu and (3) $(\text{LH}_{-1})\text{Cu}$: copper coordinated to the catechol moiety; (4) $(\text{LH}_{-1})\text{Cu}_2$: one copper at each end of the molecule; (5) $(\text{LH}_{-1})_2\text{Cu}_3$ and (6) $(\text{LH}_{-1})_3\text{Cu}_2$: oligonuclear species with copper acting as bridges between adjacent caffeate moieties.

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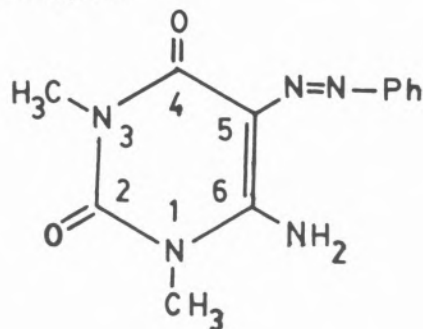
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INTERACTION OF 6-AMINO-1,3-DIMETHYL-5-PHENYLAZOURACIL WITH Co(II), Ni(II), Cu(II) AND Ag(I) IONS

INTRODUCTION

Compounds containing pyrimidine rings are widely distributed in living cells and play a significant role in many biological systems (the ring system being an integral part of several nucleic acids, vitamins, etc.); these facts have stimulated research into the coordination modes of pyrimidines, in order to know the role of metal ions in such systems [1-4]. As an arylazo group is of interest in promoting potential antineoplastic activity [5], the pyrimidine molecules having an arylazo group are of interest. For this reason and as part of our work on the interaction of pyrimidine-derived ligands with metal ions [6-9], in the present paper, the synthesis, spectroscopic characterization and thermal behaviour of the 6-amino-1,3-dimethyl-5-phenylazouracil (DZH) and its Co(II), Ni(II), Cu(II) and Ag(I) complexes have been investigated.



DZH