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Synthesis and characterization of mixed ligand complexes of zinc (II) with uridine and amino acids#

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Abstract. Mixed ligand complexes of zinc(II) with uridine and aminoacids *L*-alanine, *L*-phenylalanine and L-tryptophan were synthesized and characterized by elemental analysis, conductivity data, electronic, IR, ^{1}H-NMR and ^{13}C-NMR spectra. In these complexes, the nucleoside (uridine) acts as a monodentate ligand coordinating through O(4) under conditions of investigation whereas the aminoacids coordinate through carboxylate oxygen and amino nitrogen. The results drawn about binding sites of these octahedral complexes are compared with the results obtained from solution studies for a comprehensive understanding of the binding sites in these systems.

Keywords. Mixed ligand complexes; zinc; uridine; *L*-aminoacids.

1. Introduction

Metal ion mediated reactions involving nucleic acid constituents and amino acid side chains were the subject matter of several investigations in the recent past [1–6]. These reactions provide an opportunity to identify the nature of such interactions *in vivo* as they serve as models for many metalloenzyme reactions. Among the nucleosides (purines and pyrimidines) pyrimidines are considered simple as far as their interaction with metal ions are concerned since they possess fewer coordination sites compared to purines. However, even pyridimidine nucleosides were found to exhibit complex behaviour [7]. Uridine (figure 1) poses a special problem since its coordinating tendencies are highly *p*H dependent. It contains three potential metal ion binding sites *viz.*, O(2), N(3) and O(4). The dissociation of a proton from N(3) occurs only at high *p*H ($\sim$ 9·0), leaving the other two as viable alternate sites for metal ion binding. Among the two, O(4) is preferred as it possesses high electron density [8,9] compared to O(2) and also owing to steric hindrance of O(2) by the sugar moiety. Further, it was observed [3] that uridine shows discriminating tendencies towards stacking interactions—a phenomenon of biological significance. In order to gain an insight into such interactions it was thought important to investigate the interaction of pyrimidine nucleosides and amino acids with the biologically important metal ion Zn. The synthesis of mixed ligand complexes of Zn(II) with cytidine and aminoacids were reported recently [10]. In this manuscript the studies were extended to uridine in view of its unique behaviour. The complexes were characterized based on elemental analysis, conductivity data,

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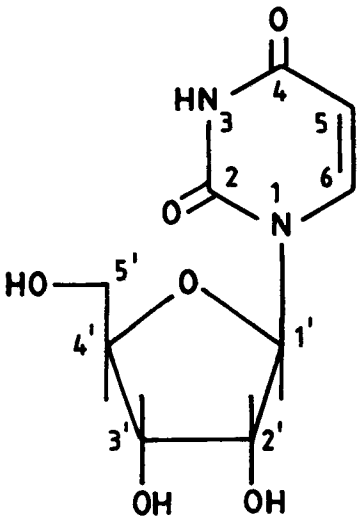


Figure 1. Molecular structure of uridine

electronic spectra, IR, ^{1}H-NMR, ^{13}C-NMR spectra and their bonding modes assigned. The conclusions are compared with solution data for a more comprehensive understanding of the reaction sites and their impact on biologically relevant processes.

2. Experimental

2.1 *Materials*

Uridine (urd), *L*-alanine (*L*-ala), *L*-phenylalanine (*L*-phe) and *L*-tryptophan (*L*-trypt) were obtained from the Sigma Chemical Company (USA). BDH AnalaR grade zinc chloride was used as supplied.

2.2 *Physical measurements and analysis*

2.2a ^{1}*H-NMR and* ^{13}*C-NMR spectra*

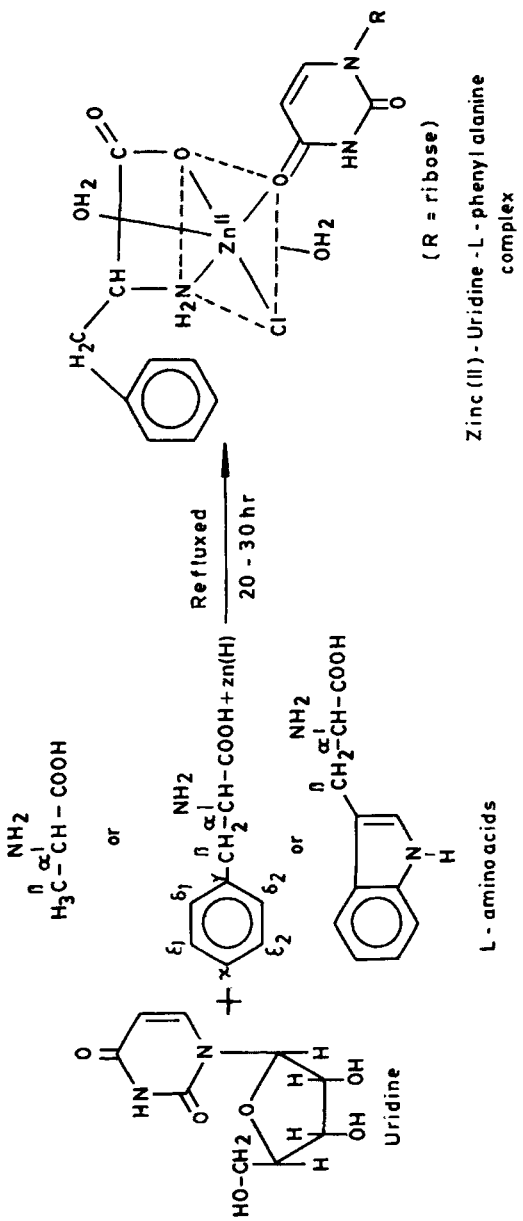
^{1}H-NMR spectra were recorded at room temperature (20–25°C) on a BRUKER AM 300/MHz pulsed FT NMR spectrometer in D_2O which was also used as an internal standard. The proton decoupled ^{13}C-NMR spectra were recorded at room temperature (20–25°C) on a VARIAN UNITY – 400/MHz and VARIAN GEMINI – 200/MHz Spectrometer operating in FT mode with 1,4-dioxan and DSS ('O' ppm) (sod-2,2-dimethyl-2-silapentane-5-sulphonate) as an external reference.

2.2b *IR, electronic spectra and conductivity data* The IR spectra were recorded (in KBr discs) on infrared spectrophotometers—IR-435, SHIMADZU in the 4000–400 cm^{-1} region and Perkin Elmer FTIR. Far infrared spectra in the region 800–200 cm^{-1} were recorded on a Perkin Elmer model 1430. The electronic spectra of the complexes were recorded in DMSO/water on SHIMADZU UV-160-A spectrophotometer. Conductivity measurements were performed using Digisun, Digital conductivity bridge (Model: DI-909) and a dip type cell calibrated with KCl solutions.

2.2c *Elemental analysis* Carbon, hydrogen and nitrogen analysis were obtained from micro analytical Perkin Elmer 240 C elemental analyser while the metal analysis was carried out on a AAS, Perkin-Elmer 2380.

2.3 *Synthesis of metal complexes*

The three complexes were synthesized by mixing an aqueous solution containing equimolar ratios of *L*-alanine (1·454 mmol) and uridine, *L*-phenylalanine (1·476 mmol) and uridine, and *L*-tryptophan (0·731 mmol) and uridine which were added simultaneously and independently to equimolar concentrations of zinc chloride.



The above three types of mixtures were refluxed on a heating mantle up to 10–20 h during which the colourless solutions changed to a golden yellow colour (ppt not obtained). The golden yellow coloured solutions were further refluxed for another 10–15 h during which they changed to brown colour solutions. The solutions were filtered and the filtrates were concentrated to half of the original volumes and kept aside for about two months. Reduced pressure was not applied in order to grow crystals. Beautiful golden yellow (brown) coloured crystals were obtained which were filtered and purified by recrystallisation from methanol solvent. The purity of these compounds was established by TLC in a mixture of solvents of methanol-ethylacetate in 1:4 ratio.

2.4 *Solution studies*

The equilibrium involved in the dissociation of uridine is represented as

$$HL \overset{K_a}{\rightleftharpoons} L^- + H^+. \tag{1}$$

The ionization constants of neutral *L*-alanine or *L*-phenylalanine or *L*-tryptophan are related to the usual equilibrium dissociation as

$$HA \overset{K_a}{\rightleftharpoons} A^- + H^+ \tag{2}$$

to determine the stability constant of the zinc(II)-uridine system. The following equations were used (charges omitted for clarity)

$$M + HL \rightleftharpoons ML + H^+ \tag{3}$$

together with related equilibria

$$M + L \overset{K_{ML}^M}{\rightleftharpoons} ML. \tag{4}$$

To determine the stability constants of the binary complexes of zinc(II) with *L*-alanine or *L*-phenylalanine or *L*-tryptophan, the following equations were used,

$$M + HA \rightleftharpoons MA + H^+ \tag{5}$$

or

$$M + A \overset{K_{MA}^M}{\rightleftharpoons} MA\,. \tag{6}$$

Table 1. Analytical and physical data of the complexes.

Complex	Found (Calcd.)% Carbon %	Hydrogen %	Nitrogen %	Metal %	Λ_M $ohm^{-1}cm^{-1}mol^{-1}$ (in DMSO)
[Zn(urd)(L-ala)$(H_2O)_2$Cl], 1 [$ZnC_{12}H_{22}N_3O_{10}Cl$]	30·14 (30·63)	4·42 (4.68)	8·32 (8·93)	13·37 (13·90)	16
[Zn(urd)(L-phe)$(H_2O)_2$Cl], 2 [$ZnC_{18}H_{26}N_3O_{10}Cl$]	40·05 (39·54)	4·58 (4.76)	7·88 (7·69)	11·63 (11·97)	15
[Zn(urd)(L-trypt)$(H_2O)_3$Cl], 3 [$ZnC_{20}H_{29}N_4O_{11}$]Cl	40·49 (39·78)	4·67 (4.81)	9·12 (9·28)	10·38 (10·84)	51

Table 2. Some characteristics IR bands (cm^{-1})

Ligand/Complex No.	υ(NH_3)(AA) asy	υ(NH_3)(AA) sy	υC(2)=O	υC(4)=O	υ(N–H) υ(C=N)	υ(COO) asy	υ(COO) sy	Non-ligand bands $P_\gamma(H_2)$	υ(M–N)	υ(M–O)	υ(M–Cl)
Free uridine, 1 $[C_9H_{12}N_2O_6]$,	—	—	1678(s)	1396(s)	1472(s)	—	—	—	—	—	—
Free L-alanine, 2 $[C_3H_7NO_2]$,	3088(m)	2950(m)	—	—	—	1597(s)	1412(s)	—	—	—	—
[Zn(urd)(L-ala)$(H_2O)_2$Cl], 3 $[ZnC_{12}H_{22}N_3O_{10}Cl]$,	3224(br)	2943(br)	1689(m)	1349(m) 1378(m)	1467(s)	1620–1640(sh)	1414(m)	847(w)	560(m)	410(m)	310(m)
Free L-phenylalanine, 4 $[C_9H_{11}NO_2]$	3065(m)	2956(m)	—	—	—	1625(sh) 1562(s)	1410	—	—	—	—
[Zn(urd)(L-phe)$(H_2O)_2$Cl], 5 $[ZnC_{18}H_{26}N_3O_{10}Cl]$	3160(br)	2940(sh)	1687(br)	1333(w)	1470(m)	1660(br)	1407(m)	860(w)	560(m)	410(m)	285(sh)
Free L-tryptophan, 6 $[C_{11}H_{12}N_2O_2]$	3037(s)	2954(M)	—	—	—	1565(s)	1410(s)	—	—	—	—
[Zn(Urd)(L-trypt)$(H_2O)_3$]Cl, 7 $[ZnC_{20}H_{29}N_4O_{11}]Cl$	2950–3150(br)	3043(br)	1720(m)	1352(m)	1465(w)	1665–1700(br)	1408(m)	906(w)	520(m)	420(m)	—

s = strong; m = medium; w = weak; br = broad; sh = shoulder

For the calculation of the stability constants of ternary zinc(II)–uridine and aminoacid complexes the following equations were used,

$$M + HL + HA \rightleftharpoons MLA + 2H^+ \tag{7}$$

$$M + L + A \overset{K^M_{MLA}}{\rightleftharpoons} MLA. \tag{8}$$

The experimental method consisted of potentiometric titration of the free ligands and of solutions containing metal ion, nucleoside (uridine) and aminoacids (*L*-alanine, *L*-phenylalanine and *L*-tryptophan) in a 1:1:1 ratio at $35 \pm 0{\cdot}1$°C with standard sodium hydroxide solution. For binary systems, a 1:1 ratio was maintained. The experimental conditions maintained were the same as those described earlier [11].

2.4a *Calculations*

The ionization constants of various ligands were calculated using the computer program PKAs [12]. All the formation constants were subjected to refinement using the computer program BEST [13]. BEST was also used to generate complete species distribution curves at various *p*H values. The refinement of the stability constants of ternary systems was done by considering all possible species present in the solution, i.e., HL^+, HA, L^-, L, A^-, ML, ML_2, MA, MA_2 and MAL. The error limits in these constants were minimised (Sigma fit = 0·001).

3. Results and discussion

The analytical and conductivity data of the complexes are presented in table 1. The analytical data corresponds with metal-uridine-aminoacid ratio of 1:1:1 and with two moles of water per mole of Zn(II) in complex 1 and 2 and three moles of water in complex 3. The conductivity values in DMSO/H_2O correspond to 1:1 electrolyte for complex 3 while those for 1 and 2 show that they are non-electrolytes [14]. The electronic spectra of uridine shows an absorption band at 254·2 nm in DMSO. This is due to $\pi - \pi^*$ transition in the ligand. The electronic spectra of the zinc complexes show multiple bands at 263·7, 310·4, 437·2 and 1042·6 nm in complex 1 and at 263·3, 360·8, 437·8 and 1040·3 nm in complex 2 and at 264·7, 380·6, 437·2 and 1042·2 nm in complex 3 which can be assigned to MLCT bands [15] in the complexes.

The infrared spectra (table 2) of these complexes in comparison with free uridine and respective free aminoacids show characteristic band positions, band shifts and band intensities which can be correlated to monodentate uridine binding and bidentate aminoacids chelation besides metal binding through water molecules and chloride is also evidenced by the IR spectra [16–20]. The characteristic IR bands of free uridine corresponding to υC(2)=O and υ(N–H, C–N) are shown in the spectra of the complexes without any negative shifts, thus ruling out their participation in coordination. Nominal upward shifts in these vibrational frequencies are presumed to be the consequence of involvement of uridine in coordination through a different coordination site, probably the C(4)=O site. There is considerable shift in υC(4)=O(ΔυC(4)=O ~ 63 cm^{-1}) corresponding with the C(4)=O of uridine. This unambiguously suggests coordination through the respective oxygen [21–25].

As regards to chelation through aminoacids, the IR spectra exhibit significant features in υNH_2 and υCOO^- regions. It is worthwhile to mention here that the free aminoacids exist as zwitter ions ($\upsilon \overset{+}{N}H_3$ A.A.COO^-) and the IR spectra of these cannot

Table 3. ^{1}H-NMR chemical shifts in acidic medium (*p*H = 4·5–5·5) of uridine and aminoacids in the absence and presence of zinc(II)

Ligand/Complex	Aminoacids	Pyrimidine nucleoside	
		C_5H	C_6H
Free uridine, 1 $[C_9H_{12}N_2O_6]$	—	5·85(d)	7·85(d)
Free L-alanine, 2 $[C_3H_7NO_2]$	3·75(q)	—	—
$[Zn(urd)(L\text{-}ala)(H_2O)_2Cl]$, 3 $[ZnC_{12}H_{22}N_3O_{10}Cl]$	3·69(q)	5·91(d)	7·88(d)
Free L-phenylalanine, 4 $[C_9H_{11}NO_2]$	3·97(t)	—	—
$[Zn(urd)(L\text{-}phe)(H_2O)_2Cl]$, 5 $[ZnC_{18}H_{26}N_3O_{10}Cl]$	3·90(t)	5·89(d)	7·87(d)
Free L-tryptophan, 6 $[C_{11}H_{12}N_2O_2]$	4·03(t)	—	—
$[Zn(Urd)(L\text{-}trypt)(H_2O)_3]Cl$, 7 $[ZnC_{20}H_{29}N_4O_{11}]Cl$	3·92(t)	5·91(d)	7·87(d)

Solvent = D_2O (values are given in ppm); d = doublet; t = triplet; q = quartet

Table 4. ^{13}C-NMR chemical shifts in acidic medium (*p*H = 4·5–5·5) of uridine and aminoacids in the absence and presence of zinc(II).

Ligand/Complex	Aminoacids		Nucleoside moiety			
	COO^-	αC	C(2)	C(4)	C(5)	C(6)
Free uridine, 1 $[C_9H_{12}N_2O_6]$	—	—	152·0	166·016	102·198	141·799
Free L-alanine, 2 $[C_3H_7NO_2]$	175·545	50·445	—	—	—	—
$[Zn(urd)(L\text{-}ala)(H_2O)_2Cl]$, 3 $[ZnC_{12}H_{22}N_3O_{10}Cl]$	172·25	51·53	152·64	167·86	101·28	141·032
Free L-phenylalanine, 4 $[C_9H_{11}NO_2]$	176·428	58·603	—	—	—	—
$[Zn(urd)(L\text{-}phe)(H_2O)_2Cl]$, 5 $[ZnC_{18}H_{26}N_3O_{10}Cl]$,	174·23	54·944	152·53	166·98	101·25	140·772
Free L-tryptophan, 6 $[C_{11}H_{12}N_2O_2]$	177·54	57·626	—	—	—	—
$[Zn(urd)(L\text{-}trypt)(H_2O)_3]Cl$, 7 $[ZnC_{20}H_{29}N_4O_{11}]Cl$	174·02	54·68	152·84	168·76	101·783	141·01

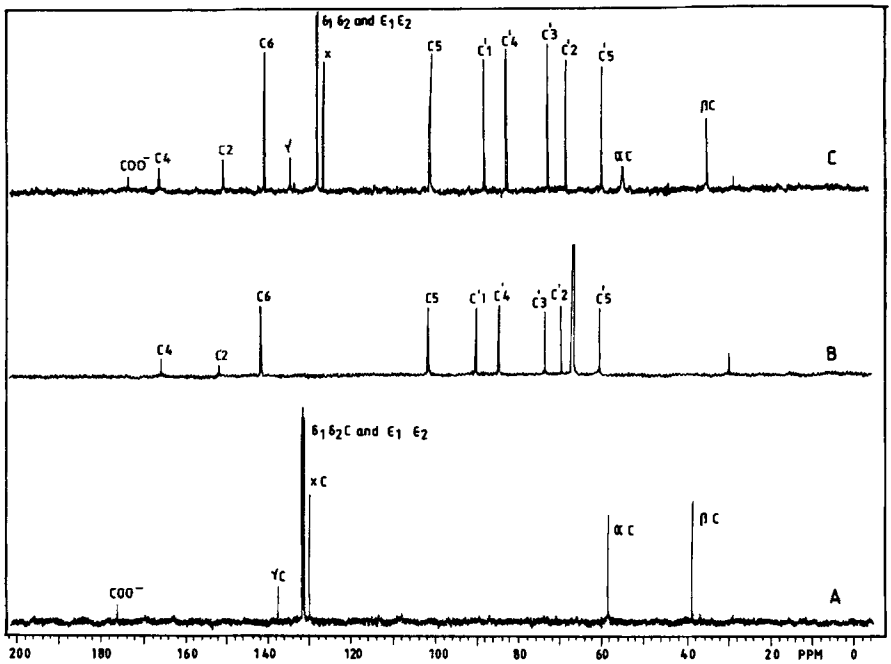


Figure 2. ^{13}C-NMR spectra of (**A**) Free *L*-phenylalanine (**B**) Free uridine (**C**) Zn(II)-uridine-*L*-phenylalanine complex in D_2O.

be compared entirely with those of metal complexes as aminoacids in metal complexes do not exist as zwitter ions; particularly free aminoacids with $\overset{+}{N}H_3$ functions show $\upsilon\overset{+}{N}H_3$ in the range of 3130–3030 cm^{-1}. In the complexes $\upsilon\overset{+}{N}H_3$ gets deprotonated and binds to metal through neutral NH_2 group. The transformation of $\upsilon\overset{+}{N}H_3$ to NH_2 must result in an upward shift in $\upsilon\overset{+}{N}H_2$ and free amino acids. At isoelectric point, they must show υNH_2 in the region 3500–3300 cm^{-1}[1,26–28]. In the present complexes, the IR spectra show characteristic bands in the region 3200–3100 cm^{-1} which is lower in comparison with free υNH_2. Hence, it can be concluded that nitrogen of the amino group is involved in coordination. The IR spectra show strong evidences in support of the involvement of carboxylate group in coordination. In comparison with free aminoacids, the υCOO (asy) shows positive shifts and υCOO^- (sym) record negative shifts which are confirmatory evidences in support of monodenticity [16,20].

Thus, it may be concluded that amino acids behave as monobasic bigentates in these complexes involving amino nitrogen and carboxylate oxygen in coordination. The spectra further show broad strong band in the region 3400–3100 cm^{-1} which can be correlated with coordination through water molecules. These broad bands show distinct structures which correspond to aminoacids as discussed earlier. The presence of coordinated water is further confirmed by non-ligand bands observed in the range 906–847 cm^{-1} due to rocking mode of coordinated water. Other low intensity bands observed in far IR region, in the range 285–560 cm^{-1} are due to υ(M–Cl), υ(M–O) and υ(M–N) stretchings [16,20]. The metal oxygen stretching frequencies could not be

assigned unambiguously due to the presence of three types υ(M–O) vibrations i.e., M–COO^-, M–H_2O and M–C(4)=O. However, the data is retained in table 2 for clarity. In complex 3 no evidence was found for the coordination of the chloride ion.

The ^1H and ^{13}C-NMR assignments in acidic medium (*p*H 4·5–5·5) are summarized in tables 3 and 4. They were identified by the literature assignments [25,29–31]. In the proton NMR spectra of the compounds, the chemical shifts of the protons of the free and metal complexes are small but significant considering the fact that the metal and ligands are in an equimolar ratio. The relatively higher shifts in the H(5) compared to H(6) resonance of uridine in the complexes indicate the involvement of O(4) in metal coordination. The 'CH' resonance of aminoacids were shifted upfield in metal complexes compared to free aminoacids since zinc will cause deprotonation of NH_3 proton on binding. The magnitude of the shifts indicate the involvement of carboxylate group in metal coordination.

The downfield shift of C(4) and no significant shifts of C(2) resonances and upfield shifts of C(5) and C(6) resonances in ^{13}C-NMR spectra of uridine in all the complexes investigated confirm the exclusive participation of O(4) in metal binding. The ^{13}C-NMR spectra of Zn(II)-urd-*L*-phe are given in figure 2. In the case of aminoacids the α'C' and carboxylate carbon resonances are significantly shifted in metal complexes thus providing definite evidence for the involvement of carboxylate and amino groups in zinc coordination.

Based on these observations, an octahedral geometry may be proposed for the complexes (structure-I).

4. Solution studies

The ionization constants of ligands along with the stability constants of binary and ternary zinc complexes are given in table 5. The species distribution curves for various systems under investigation based on the table are given in figure 3. It can be seen from the figure that the percentage of formation of various ternary complexes vary within 60–70% indicating the non-dependence of stabilities on the aromatic ring size. This is in contrast to what was observed in the case of cytidine system [10] where the dependence of stability on the aromatic ring size was observed.

Uridine is unique among the nucleosides, in the sense, that its metal binding capacity depends on the *p*H of the medium. In acidic medium it coordinates with metals through O(4) [32] and in neutral or slightly basic medium through N(3) [33], since there is little competition from protons. In neutral medium the concentration of negative charge on the oxygen atoms approximately equal that on the ring nitrogen atom [34]. However, on coordination to metal the charge distribution pattern is altered. The main effect seems to be the withdrawal of electron density from the negatively charged nitrogens and positively charged carbons with exocyclic oxygens remaining relatively unaltered [35]. This results in the metal lying in the plane of (not perpendicular) the uridine ring. Thus, the uridine ring, being non perpendicular to the metal plane, cannot take part in stacking interactions with aromatic secondary ligands. This could be the reason for the non-dependence of stabilities on the aromatic ring size which is reflected in the species distribution curves.

It is interesting and important to mention here the recent results for the interaction of metal-nucleoside-aminoacid systems [36]. The thermodynamic parameters associated with the formation of the ternary complexes involving Zn(II)-cytidine or uridine-

Table 5. Solution data* pertaining to the interaction of zinc(II) with uridine and various aminoacids [Temp = 45°C $\mu = 0{\cdot}10$ M (KNO_3)]

Ligand/Complex	pKa	Stability constants of binary complexes	Stability constants of ternary complexes
Uridine [$C_9H_{12}N_2O_6$]	9·01	4·75	—
L-alanine [$C_3H_7NO_2$]	9·37	4·98	9·51
L-phenylalanine [$C_9H_{11}NO_2$]	8·59	4·62	8·98
L-tryptophan [$C_{11}H_{12}N_2O_2$]	9·13	5·04	9·43

*The constants are accurate up to $\pm$ 0·06 pK and log K units·

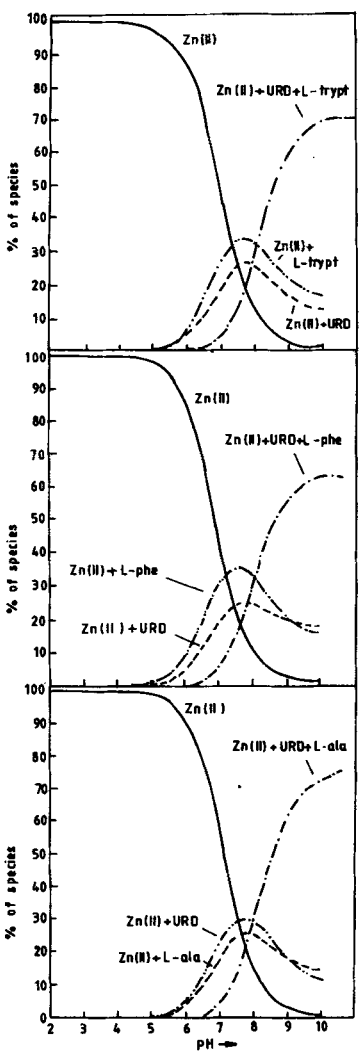


Figure 3. Species distribution curves of 1:1:1 Zn(II)-uridine-aminoacid systems at 35°C $\mu = 0{\cdot}10$ M (KNO_3).

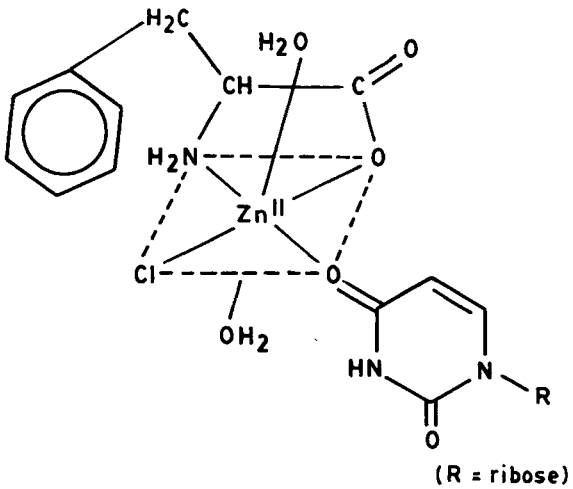


Figure 4. Tentative structure of Zn(II)-uridine-*L*-phenylalanine.

aminoacids also support the above conclusions. The ternary complexes of Zn(II)-cytidine and aminoacids seem to be favoured both by enthalpy and entropy factors. The enthalpy values for Zn(II)-cyd-*L*-ala system were lower than the *L*-phe and *L*-trypt systems. This was attributed to the differences in the nature of secondary ligands capable of participating in stacking interactions. However, in the case of Zn(II)-urd-aminoacids the ΔH_f° and ΔS_f° are of comparable magnitude, indicating the absence of any additional contribution from the secondary ligands.

The above results emphasize the importance of stacking interactions and show how the ligands with slight variations may have discriminating tendencies toward it.

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