

Synthesis and characterization of mixed ligand complexes of bio-metals with pyrimidine nucleoside (uridine) and amino acids

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Abstract. The mixed ligand complexes of Cu(II), Ni(II) and Co(II) with uridine and amino acids, L-alanine, L-phenylalanine and L-tryptophan were synthesized and characterized by elemental analysis, conductivity data, infrared spectra, electronic spectra and magnetic susceptibility data. In these complexes, the nucleoside (uridine) acts as a monodentate ligand coordinating through O(4) under the conditions of investigation, whereas the amino acids coordinate through the carboxylate oxygen and the amino nitrogen. Distorted octahedral geometry for Cu(II) and octahedral geometries for both Ni(II) and Co(II) are proposed.

Keywords. Mixed ligand complexes; divalent complexes of Cu, Ni and Co; uridine; L-aminoacids.

1. Introduction

Metal ion-mediated reactions involving nucleic acid constituents and amino acid side chains have been the subject of several investigations^{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 pyrimidine nucleosides are found to exhibit complex behaviour⁷. Uridine is unique since its coordinating tendencies are highly pH 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 a high pH (~9.0) leaving the other two as viable alternate sites for metal ion binding at biological pH. Among these two, O(4) is preferred as it possesses high electron density^{8,9} compared to O(2). In order to gather more information, we thought it was important to investigate the interaction of uridine and amino acids with the biologically important metal ions, Cu(II), Ni(II) and Co(II). The mixed ligand complexes of Zn(II) with pyrimidine nucleosides and amino acids were reported recently^{10,11}. The complexes were characterized based on elemental analysis, conductivity data, infrared spectra, electronic spectra and magnetic susceptibility data and their bonding modes assigned. Uridine acts as a monodentate ligand with exclusive O(4) binding under the conditions employed whereas the amino acids act as bidentate ligands coordinating through the carboxylate oxygen and the amino nitrogen. Distorted octahedral geometry for Cu(II) and octahedral geometries for both Ni(II) and Co(II) are proposed.

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2. Experimental

2.1 Materials

The ligands uridine (urd), L-alanine (L-Ala), L-phenylalanine (L-Phe) and L-tryptophan (L-Trp), were obtained from Sigma Chemical Company (USA). All the metal ions Cu(II), Ni(II) and Co(II) were of Analar grade (BDH). They were used in the form of chlorides without further purification.

2.2 Physical measurements and analysis

2.2a Infrared spectra and conductivity data: IR spectra were recorded (as KBr discs) on infrared spectrophotometers; IR-435 Shimadzu in the 4000–400 cm^{-1} region, and a Perkin–Elmer for FTIR. Far infrared spectra in the region 800–200 cm^{-1} were recorded on a Perkin–Elmer 1430. Conductivity measurements were performed using a Digisun Digital conductivity bridge (model: DI-909) and a dip-type cell calibrated with KCl solution.

2.2b Electronic spectra and magnetic susceptibility data: The electronic spectra of the complexes were recorded in DMSO/H₂O on a Shimadzu UV-160A spectrophotometer. The magnetic susceptibilities of the complexes were recorded on a Faraday balance (Cahn-7550-03) at room temperature using Hg[Co(CNS)₄] as the standard.

2.2c Elemental analysis: Carbon, hydrogen and nitrogen analyses were obtained on a microanalytical Perkin–Elmer 240C elemental analyser while metal analysis was carried out on an atomic absorption spectrometer, Perkin–Elmer 2380. The presence of chlorides is established by decomposing the complexes and titrating the liberated chlorides with AgNO₃.

2.3 Synthesis of metal complexes

2.3a Copper complexes: (i) Equimolar (1.17 mmols) aqueous solutions of L-alanine (L-Ala) and uridine (urd) were added simultaneously to another aqueous solution containing 1.17 mmol of copper chloride. (ii) Similarly, equimolar (1.17 mmols) aqueous solutions of L-phenylalanine (L-Phe) and uridine (urd) were added simultaneously to another aqueous solution containing 1.17 mmol of copper chloride. (iii) Finally, equimolar (0.58 mmols) aqueous solutions of L-tryptophan (L-Trp) and uridine (urd) were added simultaneously to another aqueous solution containing 0.58 mmol of copper chloride. The above mixtures were refluxed on a heating mantle (~18 h) during which the colour of the solutions changed from blue to green (precipitate not obtained). These green coloured solutions were further refluxed for another 10–12 h, after which light brown coloured compounds were obtained and a precipitate started appearing. When no further precipitation was observed after a few hours, the refluxing was stopped and the precipitate was filtered and washed with water (to remove unreacted materials and impurities). The pH of the solutions was between 2 and 3. Purities of these compounds were established by TLC in a mixture of solvents, methanol and ethylacetate, in a 1:4 ratio.

2.3b Nickel complexes: (i) An aqueous solution containing 0.84 mmol of L-alanine (L-Ala) and 0.84 mmol of uridine (urd) were added simultaneously to another aqueous solution containing 0.84 mmol of nickel chloride. (ii) Similarly, aqueous solutions containing 0.84 mmol of L-phenylalanine (L-Phe) and 0.84 mmol of uridine (urd) were added simultaneously to another aqueous solution containing 0.84 mmol of nickel chloride. (iii) Finally, an aqueous solution containing 0.63 mmol of L-tryptophan (L-Trp) and 0.63 mmol of uridine (urd) were added simultaneously to another aqueous solution containing 0.63 mmol of nickel chloride. These mixtures were refluxed on a heating mantle during which the colour of the solutions changed from green to yellow (~ 22 h) (precipitate not obtained). These yellow coloured solutions were further refluxed for another 20 h, when light brown coloured compounds were obtained, which were filtered and washed with water. The *pH* of these solutions was 4. The purities of these compounds were determined by TLC in a mixture of solvents, methanol and ethylacetate, in a 1:4 ratio.

2.3c Cobalt complexes: (i) Equimolar (1.27 mmols) aqueous solutions of L-alanine (L-Ala) and uridine (urd) were added simultaneously to another aqueous solution, containing 1.31 mmol of cobalt chloride. (ii) Similarly, equimolar (0.81 mmols) aqueous solutions of L-phenylalanine (L-Phe) and uridine (urd) were added simultaneously to another aqueous solution containing 0.81 mmol of cobalt chloride. (iii) Finally, equimolar (1.69 mmols) aqueous solutions of L-tryptophan (L-Trp) and uridine (urd) were added simultaneously to another aqueous solution containing 1.69 mmol of cobalt chloride. The above mixtures were refluxed on a heating mantle during which the colour of the solutions changed from pink to yellow (~30 h) (precipitate not obtained). These yellow coloured solutions were further refluxed for another 10–12 h, when the colour of the solutions changed from yellow to green (precipitate not obtained). These were filtered and washed with water (to remove unreacted materials and impurities), and then were concentrated to half their original volumes. Beautiful dark green coloured compounds were obtained on keeping these for two months. The *pH* of the solutions was between 5 and 6. The purities of these complexes were established by TLC in a mixture of solvents, methanol and ethylacetate, in a 1:4 ratio.

3. Results and discussion

Analytical and conductivity data of the complexes are presented in table 1. The analytical data correspond to a metal–uridine–aminoacid ratio of 1:1:1 and two moles of water per mole of metal for complexes 1, 3 and 9 and three moles of water for complexes 2, 4, 5, 6, 7 and 8. The conductivity values in DMSO/H₂O correspond to 1:1 electrolytes for complexes 2, 4, 5, 6, 7 and 8, while complexes 1, 3 and 9 are non-electrolytes¹².

The infrared spectra of various mixed ligand complexes synthesized are compiled in table 2. The infrared spectra of these complexes in comparison with free uridine and the respective free amino acids show characteristic band positions, shifts and intensities, which can be correlated to monodentate uridine binding and bidentate amino acid chelation. Besides, metal binding through water molecules and chloride is also evident from the IR spectra^{13–17}. Characteristic IR bands of free uridine corresponding to $\nu_{C_2=O}$ and $\nu(N-H, C-N)$ are shown in the spectra of the complexes without any negative shifts, thus ruling out their participation in metal 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 C₄=O site. Considerable shifts in $\nu_{\text{C}_4=\text{O}}$ ($\Delta\nu_{\text{C}_4=\text{O}} \sim 36\text{--}86\text{ cm}^{-1}$) stretching frequencies, which correspond to the C₄=O of uridine of all the metal complexes, clearly indicate the involvement of C₄=O of uridine in metal coordination^{18–22,26}.

As regards chelation through aminoacids, the IR spectra exhibit significant features in the ν_{NH_2} and ν_{COO^-} regions. It is worthwhile to mention here that free aminoacids exist as zwitterions ($\overset{+}{\text{N}}\text{H}_3\text{AA.COO}^-$) and the IR spectra of these cannot be compared entirely with those of metal complexes as aminoacids in metal complexes do not exist as zwitterions. Free aminoacids with $\overset{+}{\text{N}}\text{H}_3$ functions in particular show $\nu_{\text{NH}_3^+}$ in the range of 3130–3030 cm^{-1} . In the complexes, $\overset{+}{\text{N}}\text{H}_3$ gets deprotonated and binds to metal through the neutral NH₂ group. The transformation of $\overset{+}{\text{N}}\text{H}_3$ to NH₂ must result in an upward shift in ν_{NH_2} and free aminoacids. At the isoelectric point, they must show ν_{NH_2} in the region 3500–3300 cm^{-1} ^{23–25}. In the present complexes, the IR spectra show characteristic bands in the region 3246–3150 cm^{-1} , which are lower compared to those of free ν_{NH_2} . Hence, it can be concluded that the nitrogen of the amino group is involved in coordination. The IR spectra show strong evidence in support of the involvement of carboxylate group in coordination. In comparison with free aminoacids, the ν_{COO^-} (asym) shows positive shifts and ν_{COO^-} (sym) records negative shifts, which confirm the monodenticity^{13,17} of the carboxylate group.

Table 1. Analytical and conductivity data of mixed ligand complexes of Cu(II), Ni(II) and Co(II) with pyrimidine nucleoside (uridine) and aminoacids.

Complex	Found (Calcd.) %				$\wedge M$ ($\text{ohm}^{-1}\text{ cm}^{-1}\text{ mol}^{-1}$) (in DMSO)
	Carbon	Hydrogen	Nitrogen	Metal	
[Cu(urd)(L-Ala)(H ₂ O) ₂ Cl], 1 [CuC ₁₂ H ₂₂ N ₃ O ₁₀ Cl]	31.06 (30.75)	4.22 (4.69)	9.28 (8.97)	13.11 (13.57)	015
[Cu(urd)(L-Phe)(H ₂ O) ₃ Cl], 2 [CuC ₁₈ H ₂₈ N ₃ O ₁₁ Cl]	38.01 (38.41)	5.21 (4.98)	7.74 (7.47)	11.02 (11.29)	081
[Cu(urd)(L-Trp)(H ₂ O) ₂ Cl], 3 [CuC ₂₀ H ₂₇ N ₄ O ₁₀ Cl]	41.81 (41.14)	4.34 (4.63)	9.98 (9.59)	10.39 (10.89)	007
[Ni(urd)(L-Ala)(H ₂ O) ₃ Cl], 4 [NiC ₁₂ H ₂₄ N ₃ O ₁₁ Cl]	29.12 (29.91)	4.46 (4.98)	8.12 (8.72)	12.58 (12.19)	095
[Ni(urd)(L-Phe)(H ₂ O) ₃ Cl], 5 [NiC ₁₈ H ₂₈ N ₃ O ₁₁ Cl]	39.23 (38.74)	5.19 (5.02)	7.21 (7.53)	10.02 (10.53)	081
[Ni(urd)(L-Trp)(H ₂ O) ₃ Cl], 6 [NiC ₂₀ H ₂₉ N ₄ O ₁₁ Cl]	40.02 (40.23)	4.36 (4.86)	9.11 (9.39)	9.34 (9.84)	041
[Co(urd)(L-Ala)(H ₂ O) ₃ Cl], 7 [CoC ₁₂ H ₂₄ N ₃ O ₁₁ Cl]	30.11 (29.89)	4.44 (4.98)	9.32 (8.72)	12.94 (12.24)	104
[Co(urd)(L-Phe)(H ₂ O) ₃ Cl], 8 [CoC ₁₈ H ₂₈ N ₃ O ₁₁ Cl]	39.41 (38.72)	5.09 (5.02)	7.01 (7.53)	10.12 (10.57)	127
[Co(urd)(L-Trp)(H ₂ O) ₂ Cl], 9 [CoC ₂₀ H ₂₇ N ₄ O ₁₀ Cl]	42.14 (41.46)	4.37 (4.66)	9.16 (9.67)	10.72 (10.18)	032

Table 2. Infrared spectral data of mixed ligand complexes of Cu(II), Ni(II) and Co(II) with pyrimidine nucleoside (uridine) and aminoacids.

	u(NH ₂)(AA)			u(COO ⁻)			Non-ligand bands				
	Asym	Sym	u(C ₂ =O)	u(C ₄ =O)	u(C=N)	Asym	Sym	P _g (H ₂ O)	u(M-N)	u(M-O)	u(M-Cl)
⁹ H ₁₂ N ₂ O ₆]	-	-	1678 (s)	1396 (s)	1472 (s)	-	-	-	-	-	-
L-alanine	3088 (m)	2950 (m)	-	-	-	1597 (s)	1412 (s)	-	-	-	-
³ H ₇ NO ₂]											
L-phenylalanine	3065 (m)	2956 (m)	-	-	-	1625 (m)	1410 (s)	-	-	-	-
⁹ H ₁₁ NO ₂]					1562 (s)						
L-typtophan	3033 (s)	2954 (m)	-	-	-	1665 (s)	1410 (s)	-	-	-	-
¹¹ H ₁₂ N ₂ O ₂]											
L-Ala)(H ₂ O) ₂ Cl], 1	3150 (br)	2950 (w)	1660 (m)	1360 (s)	1465 (sh)	1545 (h)	-	-	555 (br)	410 (br)	305 (br)
¹² H ₂ N ₃ O ₁₀ Cl]				1320 (s)							
d)(L-Phe)(H ₂ O) ₃ Cl], 2	3175 (br)	2950 (sh)	1673 (s)	1335 (br)	1460 (w)	1550-	1406 (m)	861 (w)	560 (br)	415 (m)	-
¹⁸ H ₂₈ N ₅ O ₁₁ Cl]						1600 (br)					
L-Trp)(H ₂ O) ₂ Cl], 3	3232 (br)	2946 (m)	1680 (br)	1349 (m)	1454 (w)	1618 (br)	1403 (br)	931 (w)	560 (br)	430 (br)	315 (w)
²⁰ H ₂₇ N ₄ O ₁₀ Cl]											
L-Ala)(H ₂ O) ₃ Cl], 4	3201 (br)	2952 (br)	1675 (br)	1349 (w)	1465 (m)	1560-	1408 (m)	902 (w)	565 (br)	410 (w)	-
¹² H ₂₄ N ₅ O ₁₁ Cl]						1600 (br)				390 (w)	
L-Phe)(H ₂ O) ₃ Cl], 5	3193 (br)	2945 (sh)	1673 (m)	1340 (w)	1474 (m)	1540 (sh)	1410 (m)	902 (w)	560 (m)	410 (w)	-
¹⁸ H ₂₈ N ₅ O ₁₁ Cl]										395 (w)	
L-Trp)(H ₂ O) ₃ Cl], 6	3300-	2950 (br)	1673 (m)	1350 (w)	1464 (w)	1560 (sh)	1416 (m)	814 (w)	565 (m)	425 (m)	-
²⁰ H ₂₉ N ₄ O ₁₁ Cl]	3200 (br)			1310 (w)		1540 (sh)				460 (m)	
L-Ala)(H ₂ O) ₃ Cl], 7	3175 (br)	2948 (br)	1675 (br)	1346 (w)	1465 (w)	1560 (br)	1409 (w)	896 (w)	555 (br)	405 (w)	-
¹² H ₂₄ N ₃ O ₁₁ Cl]											
L-Phe)(H ₂ O) ₃ Cl], 8	3171 (br)	2950 (sh)	1662 (m)	1340 (w)	1478 (w)	1540-	1409 (w)	815 (w)	560 (br)	415 (m)	-
¹⁸ H ₂₈ N ₅ O ₁₁ Cl]						1600 (br)					
L-Trp)(H ₂ O) ₂ Cl], 9	3246 (br)	2950 (m)	1683 (s)	1340 (sh)	1463 (w)	1630-	1391 (m)	814 (w)	560 (m)	425 (m)	290 (w)
²⁰ H ₂₇ N ₄ O ₁₀ Cl]						1660 (br)					

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

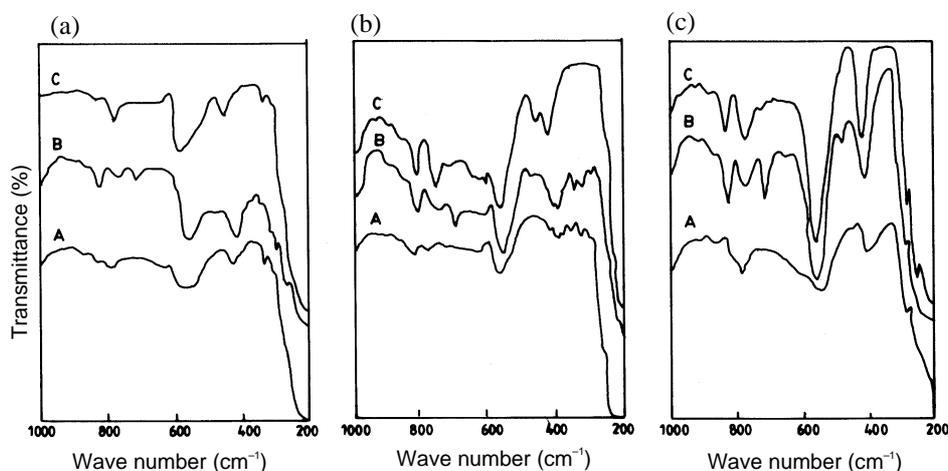


Figure 1. Far infrared spectra of (a) [Cu(urd)(L-Ala)(H₂O)₂Cl] (A), [Cu(urd)(L-Phe)(H₂O)₃]Cl (B), [Cu(urd)(L-Trp)(H₂O)₂Cl] (C); (b) [Ni(urd)(L-Ala)(H₂O)₃]Cl (A), [Ni(urd)(L-Phe)(H₂O)₃]Cl (B), [Ni(urd)(L-Trp)(H₂O)₃]Cl (C); (c) [Co(urd)(L-Ala)(H₂O)₃]Cl (A), [Co(urd)(L-Phe)(H₂O)₃]Cl (B), [Co(urd)(L-Trp)(H₂O)₂Cl] (C).

Table 3. Electronic spectra and magnetic data of mixed ligand complexes of Cu(II), Ni(II) and Co(II) with pyrimidine nucleoside (uridine) and aminoacids.

Complex	m_{ff} (BM) (temp. K)	Electronic spectral bands u_{max} (cm ⁻¹) (in DMSO/H ₂ O)
[Cu(urd)(L-Ala)(H ₂ O) ₂ Cl], 1 [CuC ₁₂ H ₂₂ N ₃ O ₁₀ Cl]	2.01 (301)	13,020 (768.0 nm); 22,421 (446.0 nm); 38,314 (261.0 nm)
[Cu(urd)(L-Phe)(H ₂ O) ₃]Cl, 2 [CuC ₁₈ H ₂₇ N ₃ O ₁₁]Cl]	2.05 (301)	13,271 (753.5 nm); 20,000 (500.0 nm); 38,314 (261.0 nm)
[Cu(urd)(L-Trp)(H ₂ O) ₂ Cl], 3 [CuC ₂₀ H ₂₇ N ₄ O ₁₀ Cl]	3.43 (301)	16,666 (600.0 nm); 26,455 (378.0 nm); 38,008 (263.1 nm)
[Ni(urd)(L-Ala)(H ₂ O) ₃]Cl, 4 [NiC ₁₂ H ₂₄ N ₃ O ₁₁]Cl]	2.69 (301)	12,896 (775.4 nm); 14,619 (684.0 nm); 23,255 (430.0 nm); 39,339 (254.2 nm)
[Ni(urd)(L-Phe)(H ₂ O) ₃]Cl, 5 [NiC ₁₈ H ₂₈ N ₃ O ₁₁]Cl]	3.11 (301)	13,051 (766.2 nm); 14,465 (691.3 nm); 23,809 (420.0 nm); 38,167 (262.0 nm)
[Ni(urd)(L-Trp)(H ₂ O) ₃]Cl, 6 [NiC ₂₀ H ₂₉ N ₄ O ₁₁]Cl]	2.61 (301)	13,368 (748.0 nm); 14,836 (674.0 nm); 25,641 (390.0 nm); 37,593 (266.0 nm)
[Co(urd)(L-Ala)(H ₂ O) ₃]Cl, 7 [CoC ₁₂ H ₂₄ N ₃ O ₁₁]Cl]	4.08 (301)	11,098 (901.0 nm); 14,760 (677.4 nm); 16,276 (614.4 nm); 38,314 (261.0 nm)
[Co(urd)(L-Phe)(H ₂ O) ₃]Cl, 8 [CoC ₁₈ H ₂₈ N ₃ O ₁₁]Cl]	4.09 (301)	11,187 (894.0 nm); 14,738 (678.5 nm); 16,273 (614.5 nm); 38,610 (259.0 nm)
[Co(urd)(L-Trp)(H ₂ O) ₂ Cl], 9 [CoC ₂₀ H ₂₇ N ₄ O ₁₀ Cl]	4.87 (301)	11,298 (885.1 nm); 14,753 (677.8 nm); 16,291 (613.8 nm); 37,453 (267.0 nm)

Thus, it may be concluded that aminoacids act as monobasic bidentates in these complexes coordinating through amino nitrogen and carboxylate oxygen^{14-16,24-28}. The spectra further show broad strong bands in the region 3400–3100 cm⁻¹, which are attributed to the coordination of 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 931–814 cm⁻¹ due to the rocking mode of coordinated water molecules. Other low intensity bands observed in far-IR region (figure 1) in the range 565–290 cm⁻¹ are due to $\nu(\text{M-Cl})$, $\nu(\text{M-O})$ and $\nu(\text{M-N})$ stretch^{13,17}. The metal–oxygen stretching frequencies could not be assigned unambiguously due to the presence of three types of $\nu(\text{M-O})$ vibrations i.e., M–COO⁻, M–H₂O and M–C₄=O. However, the data are retained in table 2 for clarity. In complexes 2, 4, 5, 6, 7 and 8 no evidence was found for the coordination of the chloride ion.

The magnetic data pertaining to these systems are given in table 3. The magnetic moments 2.01, 2.05 and 2.43 BM of Cu(II) complexes 1, 2 and 3 are indicative of one unpaired electron each in these systems^{28,29}. The magnetic data of Ni(II) complexes 4, 5 and 6 show magnetic moments of 2.63, 3.11 and 2.61 BM, which are close to that of an octahedral d^8 system with two unpaired electrons^{28,29}. The magnetic susceptibilities of Co(II) complexes 7, 8 and 9 show magnetic moment values of 4.08, 4.09 and 4.37 BM, and suggest high spin octahedral geometry with three unpaired electrons in these complexes^{28,29}.

The electronic spectral data of various complexes are presented in table 3. The electronic spectra of uridine show an absorption band at 254.2 nm in DMSO. This is assigned to the $p-p^*$ transition of the free ligand. The electronic spectra of complexes 1, 2 and 3 show multiple bands, which are assigned to ${}^2E_g \rightarrow {}^2T_{2g}$ and CT transition characteristics of the d^9 system. Hence, a distorted octahedral geometry was proposed for the copper complexes²⁹⁻³¹. The electronic spectra of the complexes 4, 5 and 6 show multiple bands which are assigned to ${}^3A_{2g} \rightarrow {}^3T_{2g}$, ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$, ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ and CT transitions of d^8 system. Hence, octahedral geometry was proposed for all the nickel

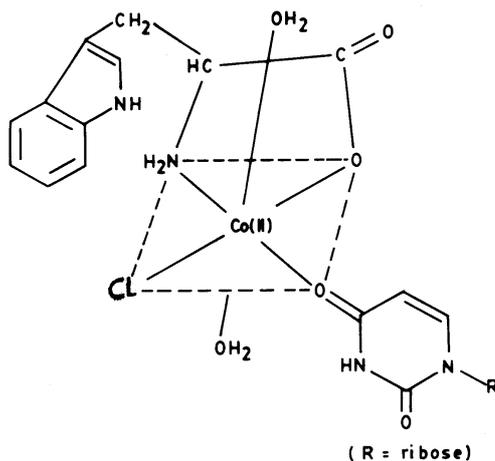


Figure 2. Structure of [Co(urd)(L-Trp)(H₂O)₂Cl].

complexes²⁹⁻³¹. The electronic spectra of complexes 7, 8 and 9 show multiple bands which are assigned to ${}^4T_{1g} \rightarrow {}^4T_{2g}(F)$, ${}^4T_{1g} \rightarrow {}^4T_{1g}(P)$, ${}^4T_{1g} \rightarrow {}^4A_{2g}$ and CT transitions of the d^7 system. Therefore, octahedral geometry (figure 2) was proposed for cobalt complexes^{29,31}.

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