

Synthesis and Thermal Study of Co (II), Ni (II), Cu (II) Mixed Ligand Complexes Using Histidine As Tridentate Ligand

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Abstract: The mixed ligand complexes of Co (II), Ni (II) and Cu (II) with histidine (His.) and 8-hydroxyquinoline (Qui.) have been synthesized and characterized. The resulting complexes were characterized by vibrational and electronic spectral data, thermogravimetric studies, metal analysis and molar conductance measurements. The histidine acts as tridentate ligand, coordinating through the two nitrogen atoms of imidazole ring and the amino group and carboxylate oxygen whereas 8-hydroxyquinoline shows a bidentate nature and the coordination occurs through nitrogen of imine group and oxygen of phenol group. The experimental data suggest that a mononuclear octahedral structure with general formula $[M(\text{His.})(\text{Qui.})\text{H}_2\text{O}]$ where $M = \text{Co (II), Ni (II)}$ and $[\text{Cu}(\text{His.})(\text{Qui.})\text{H}_2\text{O}] \cdot \text{H}_2\text{O}$, thermo gravimetric studies reveal the presence of coordinated water molecules in all complexes. The molar conductance measurements reveal non-electrolytic nature of complexes.

Keywords: Histidine, 8-hydroxyquinoline, mixed ligand complexes.

I. INTRODUCTION

Mixed ligand complexes containing amino acid as coligand are potential biomimetic models for metal-protein interaction.^[1] Research has shown significant progress in utilization of transition metal complexes as drugs to treat several human diseases like carcinomas, infection control, anti-inflammatory, diabetes and neurological disorders.^[2] The geometry, number of ligands, donor groups, nature of binding i.e. microcoordination environment is the key to the understanding specific physiological function.^[3] Histidine is a tridentate ligand that has an amino, imidazole, and carboxylate group as metal ion binding sites, but only a metal ion with an octahedral coordination sphere can form a tridentate chelate.^[4] Imidazole group plays important role in numerous bioactive compounds and pharmacological interest of the imidazole ring has already been established. It acts as proton donor/acceptor and charge transfer agent and is ligated to the metal ions in B₁₂ coenzyme.^[5] Ternary complexes of histidine and threonine are dominant in human serum and are important in relation to the transport of copper in blood.^[6] Mixed ligand amino acid complexes are also of relevance in enzyme inhibition.^[7]

A pharmacological and toxicological property of amino acid complexes is another area that has drawn lot of current attention.^[8-9] It has been found that metal complexes of Co (II) and Ni (II) with 8-hydroxyquinoline possess antibacterial and antifungal activity.^[10] Some mixed ligands complexes of Co(II) and Fe(III) ions with malonic acid as primary and heterocyclic bases viz. quinoline, iso quinoline, 8-hydroxyquinoline, pyridine, 2-aminopyridine and 2-aminophenol as secondary ligands have been prepared and their antimicrobial studies have been evaluated, the complexes containing 8-hydroxyquinoline as secondary ligand were much more microbial activity than other complexes.^[11]

Mixed ligand complexes of 8-hydroxyquinoline and o-hydroxybenzylidene-1-phenyl-2, 3-dimethyl-4-amino-3-pyrazolin-5-on with Fe (II), Co (II), Ni (II) and Cu (II) ions were synthesized, the molar conductivity of the complexes in DMF solution have non-electrolyte behavior and 8-hydroxyquinoline coordinate through the nitrogen and oxygen atoms. therefore, the complexes have tetrahedral configuration.^[12] Several mixed ligand Ni(II), Cu(II) and Zn(II) complexes of 2-amino-3-hydroxypyridine(AHP) and imidazoles viz., imidazole (him), benzimidazole (bim), histamine(hist) and L-histidine(his) have been synthesized and characterized, the geometry becomes tetrahedral when mixed ligand complexes are formed with him, bim and hist for Cu(II) and Zn(II). All Ni (II) and Cu (II) / Zn (II) histidine mixed ligand complexes have octahedral geometry. The complexes exhibited considerable amount of antibacterial activity and Cu (II) complexes cleave DNA yielding scission of the sugar-phosphate backbone.^[13] Mixed ligand Zr(IV) complexes prepared with 8-hydroxyquinoline as a primary ligand and amino acids such as L-alanine/L-serine/glycine as a secondary ligand. Zr(II) was used due to its high coordination number and ability to form stable complexes. These complexes were characterized and screened for their antibacterial, antifungal and cytotoxic properties.^[14] Kinetics and mechanism of thermal decomposition of o-vanilline-L-histidine complexes of some transition metal ions in which histidine acts as a tridentate ligand and an octahedral structure for the complexes has been reported.^[15] Synthesis, structural, coordination and thermal stability studies of mixed ligand complexes of histidine with other ligands (adenine/guanine/ethylenediamine, diethylenetriamine or N,N,N',N''-pentamethyldiethylenetriamine, glycine or L-alanine, histamine and diethylglyoxime) have been carried out.^[16-18]

In this work, we report the preparation and characterization of mixed ligand complexes with histidine as tridentate and 8-hydroxyquinoline as bidentate ligands.

II. EXPERIMENTAL

2.1 Chemicals

Chemical reagents and starting materials were obtained from Fluka and BDH.

2.2 Synthesis of mixed ligand complexes

A solution of histidine was prepared by dissolving it in one equivalent of sodium hydroxide. The solution of 8-hydroxyquinoline was prepared by dissolving it in ethanol. The solution of metal ions Co (II), Ni (II) and Cu (II) were prepared in one equivalent of hydrochloric acid. To prepare metal complex, the two dissolved ligands were mixed with 0.1 mol.L⁻¹ metal ion solution in 1:1:1 molar ratio at room temperature and the PH >7 with total volume equal to 10 ml, the mixing started with addition of histidine to metal then followed by adding 8-hydroxyquinoline. The PH of solution was adjusted by NaOH. The color of mixture was change and refluxed for 4 hours, the colored product was collected by filtration and washed several times with 50% ethanol-water mixture and dried in an oven at 50 °C for about one day.

2.3 Instrumentation

Melting points were recorded by using Gallenkamp M.F.B. 600.01F of melting point apparatus . Infrared spectra were recorded using FTIR 8300 Shimadzu as KBr disk in the range (4000 - 600) cm⁻¹ .UV-Visible spectra were measured using Shimadzu UV-Vis 160A Ultra-violet spectrophotometer at room temperature using silica cells of 1.0 cm length. The metal percent in the prepared complexes were determined using Shimadzu 680 cc-flame. Conductivity measurements of 0.001M ethanol solution of the complexes were measured at 25 °C by BC3020 Professional Bench top conductivity meter Trans instruments.

III. Results and Discussion

The physical properties of complexes are given in table 1 in addition to the molar conductance values with 0.001M in ethanol as a solvent at room temperature 25 °C which indicating non electrolyte behavior.

Table 1: Physical data of mixed ligand complexes

Compound	Formula and name	Color and m.p.	Metal analysis Found (Calc.)	Molar Conductivity μ s	Suggested Structure
HQCo	[Co(his.)(quin.)] Histidinatoquinolino cobalt(II)	Green 200 °C	15.5 (15.6)	3.21	Octahedral
HQNi	[Ni(his.)(quin.)] Histidinatoquinolino nickel(II)	Light green 280 °C	15.4 (15.5)	17.63	Octahedral
HQCu	[Cu(his.)(quin.)] Histidinatoquinolino copper(II)	Dark green 290 °C	14.9 (15.8)	20.0	Octahedral

3.1 Ultraviolet-visible spectroscopy

The octahedral Co (II) is known to has the following three spin allowed transition (ν_1) $^4T_{1g}(F) \rightarrow ^4T_{2g}(F)$, (ν_2) $^4T_{1g}(F) \rightarrow ^4A_{2g}(F)$ and (ν_3) $^4T_{1g}(F) \rightarrow ^4T_{2g}(P)$ out of these, the first transition (ν_1) usually occurs lower frequencies and is expected to appear beyond 1000 nm in the near infrared region. The position of (ν_2) transition in Co (II) complex, however be ambiguous and is rather difficult to locate with certainty sometimes it appears as a shoulder on either side of the main absorption band (ν_3 transition), or in some cases it may not be observed at all.^[19] Thus in the present study of cobalt (II) complex, the transition obtained at 953 nm can be assigned as ν_1 transition. The main absorption band observed at 752 nm can be assigned as ν_3 transition. The position of ν_2 transition is not clear; other bands observed at 238,426 can be regarded as ligand field and charge transfer bands, respectively.

The band at 341 nm is typical ligand based transition. Ni(II) complex shows three bands with λ max value in the range 410, 740- 767 nm and around 916 nm, these bands assigned to the respective d-d transitions, $^3A_{2g}(F) \rightarrow ^3T_{1g}(P)$, $^3A_{2g}(F) \rightarrow ^3T_{1g}(F)$, $^3A_{2g}(F) \rightarrow ^3T_{2g}(F)$ with Ni(II) ion the octahedral ligand field.^[5] The electronic spectrum of Cu (II) shows d-d transition at 680 nm { $^2E_g \rightarrow ^2T_{2g}(F)$ transition } is more consistent with octahedral geometry.^[5]

3.2 Infrared spectra of complexes

The characteristic vibrations modes of mixed ligand complexes are described in table 2. IR spectra of HQCo (m.p 200 °C), HQNi (m.p 280 °C) and HQCu (290 °C) complexes show a broad band in the range of 3450-3435 cm⁻¹ followed by another band in the range 800- 817 cm⁻¹, which is due to characteristic of ν OH of coordinated water. An important feature of infrared spectra of the metal complexes with Qui. is the absence of O-H stretching vibration of the free phenol group O-H appear about 3150 cm⁻¹ region. A presence of ν (C-O) band at 1215 cm⁻¹ in Qui. spectrum, shifting to the higher frequencies between 7-19 cm⁻¹ in the spectrum of

mixed ligand complexes, indicating the coordination of phenolic oxygen to metal ion.^[10] The $\nu(\text{C}=\text{N})$ band observed at 1575 cm^{-1} in the spectrum of Qui. ligand, this band reduced in intensity with shifting to lower wave number 1537 cm^{-1} in the spectra of complexes, this indicates the coordination through nitrogen donor of Qui. with the metal.^[13]

In amino acid νNH_3^+ appears in $3130\text{-}3030\text{ cm}^{-1}$ region.^[20] In the spectrum of His. it appears at 3082 cm^{-1} but overlaps with other vibrations such as νNH (imidazole group) and νCH (heterocyclic + νCH_2 group \square 3016 cm^{-1}). Theoretically νNH_3^+ should vanish on coordination. In metal complexes, however, some broad band appears at \square 3300 cm^{-1} , which must be arising from other vibrations appearing in this region.^[21] In His. spectrum in plane deformation $\delta(\text{NH}_3^+)$ appears at 1633 cm^{-1} which vanishes in metal complexes. The $\nu_{\text{asym}}(\text{COO}^-)$ band of His. observed at 1633 cm^{-1} is shifted to lower wave number $1600\text{-}1625\text{ cm}^{-1}$ and the $\nu_{\text{sym}}(\text{COO}^-)$ mode observed 1413 cm^{-1} in the spectrum of His. is found to be shifted to lower wave number $1377\text{-}1380\text{ cm}^{-1}$ in the spectra of complexes indicating the coordination of carboxylic acid group via oxygen with metal. The magnitude of separation between these two vibrations ($>200\text{ cm}^{-1}$) suggests that the coordination of carboxylate group is in unidentate fashion.^[10] The imidazole exhibit a strong $\text{C}=\text{N}$ ring band in the region $1581\text{-}1577\text{ cm}^{-1}$ which is shifted to 1535 cm^{-1} in all complexes. This lower value of imidazole $\nu\text{C}=\text{N}$ indicates that imidazole nitrogen in coordination with the metal ion in all the complexes.^[5] The infrared of prepared complexes have shown weak bands in the range of $(430\text{-}474)\text{ cm}^{-1}$ and $(524\text{-}576)\text{ cm}^{-1}$ which was attributed to the $\nu(\text{M-O})$ and $\nu(\text{M-N})$ respectively.^[4, 13]

Table 2: The characteristic bands of infrared spectra of the mixed ligand complexes

Compound	$\nu(\text{O-H})$ phenol	$\nu(\text{C=N})$ imine	$\nu(\text{C-O})$ phenol	$\nu_{\text{asym}}(\text{COO}^-)$, $\nu_{\text{sym}}(\text{COO}^-)$	$\nu(\text{C=N})$ imidazole	$\nu(\text{M-N})$	$\nu(\text{M-O})$
Qui	3150	1575	1215	-	-	-	-
His	-	-	-	1633 1413	1581	-	-
HQCo	-	1537	1222	1625 1377	1535	528	440
HQNi	-	1537	1234	1600 1379	1535	576	474
HQCu	-	1537	1230	1600 1380	1535	524	430

3.3 Thermal studies

The TG and DTA studies of complexes have been recorded in the helium gas at the constant heating rate of $20\text{ }^\circ\text{C}/\text{min}$. The complexes show gradual loss in weight due to decomposition by fragmentation with increasing temperature. Thermogravimetric curve of HQCo, HQNi and HQCu complexes show the presence of coordinated water and HQCu complex also show water molecule in outer of the coordination sphere.

Thermogram of these complexes shows the loss in weight corresponding to water molecules with moiety of histidine, followed by weight loss of 8-hydroxyquinoline as well as CO_2 moieties present in the complexes.^[10,5] thermolysis data for complexes are given in table 3.

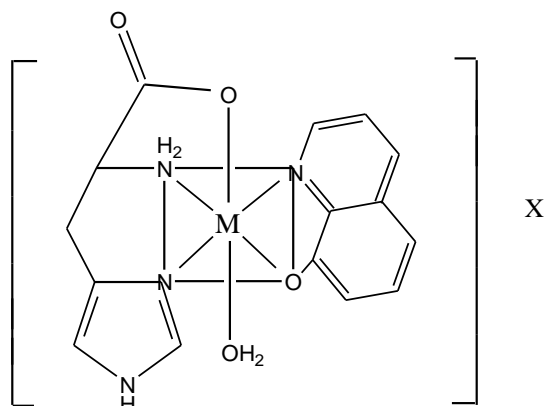
Table3: Thermolysis data for HQCo, HQNi and HQCu complexes.

NO.	Complex	Temperature range, $^\circ\text{C}$	%Weight loss		Decomposition product	Liberate part
			Found	Calcd.		
1.	$[\text{CoC}_{15}\text{H}_{16}\text{N}_4\text{O}_4]$	30-100	17.2	18.5	$[\text{CoC}_{12}\text{H}_{10}\text{N}_2\text{O}_4]$	$\text{C}_3\text{H}_6\text{N}_2$
		140-240	5.5	7.9	$[\text{CoC}_{11}\text{H}_8\text{N}_2\text{O}_3]$	$\text{H}_2\text{O}, \text{C}$
		300-400	31.7	34.2	$[\text{CoC}_2\text{H}_2\text{NO}_5]$	$\text{C}_9\text{H}_6\text{N}$
		600-730	12.4	14.8	$[\text{CoONH}_2]$	CO_2, C
2.	$[\text{NiC}_{15}\text{H}_{16}\text{N}_4\text{O}_4]$	110-190	22.7	23.2	$[\text{NiC}_{12}\text{H}_8\text{N}_2\text{O}_3]$	$\text{C}_3\text{H}_6\text{N}_2$ H_2O
		230-300	6.2	6.3	$[\text{NiC}_{10}\text{H}_8\text{N}_2\text{O}_3]$	C
		315-500	33.1	34.2	$[\text{NiCH}_2\text{NO}_3]$	$\text{C}_9\text{H}_6\text{N}$
		530-700	13.8	15.8	$[\text{NiO}]$	CO_2, NH_2
3.	$[\text{CuC}_{15}\text{H}_{18}\text{N}_4\text{O}_5]$	100-150	23.2	24.7	$[\text{CuC}_{11}\text{H}_{13}\text{N}_2\text{O}_4]$	H_2O $\text{C}_4\text{H}_5\text{N}_2$
		150-280	10.5	11.7	$[\text{CuC}_{10}\text{H}_8\text{NO}_3]$	H_2O CH_3N
		280-400	10.5	10.9	$[\text{CuC}_9\text{H}_8\text{NO}]$	CO_2
		400-800	17.5	16.7	$[\text{CuC}_5\text{H}_3\text{N}]$	$\text{C}_4\text{H}_5\text{O}$

IV. Conclusion

The evidences obtained from the above studies suggest an octahedral structure for HQCo, HQNi and HQCu with tridentate histidine ligand and bidentate 8-hydroxyquinoline ligand. The molar conductivity of

complexes has non- electrolytic nature of all complexes. Thermal analysis confirms the presence of a coordinated water molecule in all prepared complexes and water molecule out of the coordination sphere of HQCu complex.



M=Co(II),Ni(II) cobalt and nickel complexes

M=Cu(II),X=H₂O copper complex

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