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Synthesis, Characterization Thermal Studies of Copper (II) Amino Acid Complexes

Shraddha Shukla*, **Anupama Kashyap and Anil Kashyap**

Department of Chemistry, Govt. VYTPG Autonomous College Durg (c.g.), india.

ABSTRACT

The three new mixed-ligand complex of the formula $[Cu(Pro)(Meth)(H_2O)_2]$, $[Cu(Pro)(Ser)(H_2O)_2$ and $[Cu(Pro)(Tyr)(H_2O)_2$ in which proline taken as common ligand and methionine, serine or tyrosine taken as secondary ligand have been synthesized and characterized through, elemental analysis, spectroscopic, thermal analysis. A distorted octahedral structure has been proposed for all the prepared complexes.
Keywords: Mixed ligand complexes, amino acids, spectral characterization, distorted octahedral structure.

*Corresponding author

INTRODUCTION

Investigation on the complexing ability of transition metal ions with model ligands assist in the understanding of the function of physiological systems. Mixed ligand complexes are known to play an important role in biological systems [1]. Amino acids show tendency of complex formation with metals. These metal amino acid complexes have importance in the field of biological and pharmacentical [2-3]. Many enzymes are activated by some metal ions through the formation of bridge structure [4]. Metal coordination bonds provide the conformational stability to the enzyme molecules [5-8], by the interaction of metal ions with polypeptide sub units of multichain enzymes. It has been found that Copper (II) ion in Copper amino acid complexes, with its preferred square planer geometry; bind a maximum two amino acid. The possibility for Copper amino acid coordination to occur has been proved both under physiological [9] and in vitro system [10-13]. Transition metal Copper plays an important role in the oxidative DNA damage which is incorporated with aging and Cancer [14]. Some Copper (II) complexes show a variety of super -oxide dismutase activity [15]. The literature survey reveals that very limited work of solid ternary complexes of transition metals with amino acids have been reported in the past [16-22].

MATERIALS AND METHODS

An equimolar solution of proline and methionine, serine or tyrosine was heated on water bath for 2½ hr, with slight excess of freshly precipitated metal hydroxide. The hot solution was filtered. The filtered solution was then concentrated on water bath. The pH of the solution was kept 7.0 because at pH 7.0 mixed ligand complexes are predominant. In the concentrated hot solution small amount of absolute alcohol was added with constant stirring. The blue color of solid complexes was separated by slow evaporation. The formed solid complexes were recrystallized with double distilled water and dried in vacuum at 70°C.

RESULTS AND DISCUSSION

To establish the composition of the mixed ligand Copper complexes, the percentage composition of Carbon, hydrogen, nitrogen, oxygen and metal were determined. The percentage analysis is given in Table-1, are in good agreement with the stoichimetry [Cu(AB)] where,

A = Proline ($C_3H_7NO_3$)
B = Methionine ($C_5H_{11}NO_2S$)
       or
   Tyrosine ($C_9H_{11}NO_3$

The DTA curves show a three stage decomposing pattern. The pyrolysis steps are given in Table-2. The main stages are observed at 400°C,450°C and 475°C respectively for [Cu(Pro)(Ser)(H_2O)$_2$], [Cu(Pro)(Meth)(H_2O)$_2$] and [Cu(Pro)(Tyr)(H_2O)$_2$], after that the process

of oxidation and decomposition take place. After the final decomposition above 470°C, CuO is formed. Water molecule eliminated at around 170°C is coordinated water [23].

Table 1: Elemental Analysis Data

S.N	Molecular formula of complex	Color	% Analysis found (cal.)						Molecular wt. found (Cal.)
			C	H	N	O	S	M	
1	[Cu(C$_8$H$_{16}$N$_2$O$_5$)(H$_2$O)$_2$]	Blue	28.58 (30.07)	3.94 (4.39)	7.65 (8.77)	36.88 (38.01)	-	18.03 (19.73)	324.38 319.26)
2	[Cu(C$_{10}$H$_{20}$N$_2$O$_4$S)(H$_2$O)$_2$]	Blue	23.36 (33.02)	4.07 (4.95)	6.03 (7.70)	30.50 (29.38)	2.35 (2.99)	16.67 (17.34)	374.68 (363.38)
3	[Cu(C$_{14}$H$_{20}$N$_2$O$_5$)(H$_2$O)$_2$]	Blue	38.42 (42.49)	4.87 (4.55)	7.13 (7.08)	34.19 (35.60)	-	15.16 (15.93)	398.10 (395.36)

The electronic spectral data of the complexes is shown in Table-3. An asymmetric broad and weak band is observed at about 16,393 cm^{-1}, 16,000 cm^{-1} , 15,873 cm^{-1} respectively for [Cu(Pro)(Ser)(H$_2$O)$_2$], [Cu(Pro)(Meth)(H$_2$O)$_2$] and [Cu(Pro)(Tyr)(H$_2$O)$_2$]. υ_{max} and extinction coefficient ε_{max} values indicate that the geometry is tetragonally distorted octahedron [3]. The symmetry of the complexes may be assumed as D$_4$h in which N atom are taken equivalent to O atoms. The complex does not undergo dissociation or association, because the change in concentration of the solution does not alter the υmax.

Table 2: Thermal analysis

S.N.	Complexes	Decomposition steps and T$_{max}$/^{o}C	Wt. loss	Probable assignment
1	[Cu(Pro)(Ser)(H$_2$O)$_2$]	I – 177	11	Loss of two waters molecules
		II – 224	33	Loss of one ligand
		III – 400	60	Loss of another ligand
2	[Cu(Pro)(Meth)(H$_2$O)$_2$]	I – 100	10	Loss of two waters molecules
		II – 250	30	Loss of one ligand
		III – 450	56	Loss of another ligand
3	[Cu(Pro)(Tyr)(H$_2$O)$_2$]	I – 140	15	Loss of two waters molecules
		II – 249	30	Loss of one ligand
		III – 475	64	Loss of another ligand

IR spectra and band assignment of the Copper (II) complexes are given in Table-4. For the mixed ligand complexes the stretching vibration of υ_s(COO$^-$) and υ_{as}(COO$^-$) appear in the range 1380-1475 cm^{-1} and 1553-1665 cm^{-1}. υ_{as} (COO$^-$) band indicate the presence of two different amino acids. The coordination of nitrogen atom of the –NH$_2$ with metal ion is indicated by the shift of –NH band to 3235 cm^{-1} – 3265 cm^{-1} typical of coordinated amino group [24]. In the far IR spectra v(M-0) and v(M-N) stretching vibration modes appear in the ranges 450-485 cm^{-1} and 360-418 cm^{-1}, respectively. The range 3180-3393 cm^{-1} indicates the OH stretching vibration of coordination water. Free carboxylic (COOH) groups could not be found in IR spectral data, indicating coordination of metal ions to the carboxylate anions.

From the study of IR spectrum, it may be noted that the involved amino acids in the complexes are bidentate coordinating through the $-NH_2$ and COO^- groups.

Table 3: Electronic spectral data

S.N.	Complexes	γ_{max} (nm)	ABS	Wave number (cm^{-1})	Energy (ev)	Frequency (THz)	ε_{max}
1	[Cu(Pro)(Ser)(H$_2$O)$_2$]	619	0.278	16,393	2.04	491	52.45
2	[Cu(Pro)(Meth)(H$_2$O)$_2$]	625	0.285	16,000	1.99	479	53.68
3	[Cu(Pro)(Tyr)(H$_2$O)$_2$]	614	0.151	15,873	1.97	475	51.36

The ESR spectra of the complexes shown in Table-5 indicate that complexes are paramagnetic in nature with one unpaired electron (d^9, magnetic moment (1.81-1.84BM).

The trend $g_{11}>g_1>g_0$ observed suggests [25] the unpaired electron is localized in the $d_{x^2-y^2}$ orbital. The observed A_{11} and higher g_{11} values indicates [26] that there is slight distortion from planarity.

Table – 4: IR Spectral data of the complexes (Cm^{-1})

S.N.	Complexes	υ_s (COO$^-$)	υ_{as} (COO$^-$)	υ (NH$_2$)	υ (OH)	υ (M-O)	υ(M-N)
1	[Cu(Pro)(Ser)(H$_2$O)$_2$]	1380	1553	3235	3261	450	360
2	[Cu(Pro)(Meth)(H$_2$O)$_2$]	1432	1665	3251	3180	473	395
3	[Cu(Pro)(Tyr)(H$_2$O)$_2$]	1475	1580	3265	3393	485	418

Table 5

S.N.	Complexes	ESR Parameters						μ eff(BM)
		g_t	ge	g_{11}	g_1	A_{11}	A_1	
1	[Cu(Pro)(Ser)(H$_2$O)$_2$]	2.1200	2.1243	2.1790	2.065	115	57.5	1.84
2	[Cu(Pro)(Meth)(H$_2$O)$_2$]	2.1164	2.1274	2.1680	2.080	112	49.6	1.81
3	[Cu(Pro)(Tyr)(H$_2$O)$_2$]	2.1289	2.1294	2.1717	2.041	117	52.3	1.82

CONCLUSION

The results of elemental analysis suggest that the molecular formula of the complexes is [Cu(AB)] type. Electronic IR spectral and ESR studies suggest that these complexes have distorted octahedron geometry and the symmetry of the complexes may be D$_4$h. Magnetic measurement indicates that the complexes are paramagnetic in nature. From the thermal analysis complexes were stable up to about 400°C and they decomposed to yield pure CuO at around 700°C.

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