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Thermal Studies of New Cu (II) Amino Acid Complex.

Shraddha Shukla *, Anupama Kashyap and Anil Kashyap.

Department of Chemistry, Govt. VYTPG Autonomous College Durg (C.G.), India

ABSTRACT

A new ternary complexes of Cu(II) with amino acid have been prepared. In this proline taken as common ligand, where as glycine and lysine taken as secondary ligands. These have been characterized on the basis of elemental analysis, melting point, magnetic susceptibility and electronic spectra. The result of elemental analysis suggest that the molecular formula of the complexes is Cu(AB) $2H_2O$ type, spectral studies suggest that this complexes have octahedral geometry since single band is observed in the electronic spectra trans-geometry is proved.

Keywords: Ternary complexes, ligand, amino acids, elemental analysis, octahedral structure.

**Corresponding author*

INTRODUCTION

Copper complexes with amino acids are compounds of biological importance [1-3]. Some metal ions activated many enzymes through the formation of enzyme metal bridge structure [4]. It has been found that copper (II) ion in copper (II) amino acid ternary complexes with its preferred square planar geometry, binds maximum of two amino acids. Some Copper (II) complexes are found to exhibit a variety of pharmacological activity and super oxide dismutase activity [5]. In addition, Copper proteins containing mono- , di-, or multinuclear centers are important derivatives in several biological processes such as dioxygen transport or activation, redox processing of molecular oxygen, electron transfer, reduction of nitrogen oxides and hydrolytic chemistry [6-8]. Copper (II) binary and ternary complexes of amino acids and peptides have importance for Copper (II) binding in many biological systems [9-12]. Some ternary complexes of Copper(11) and Nickel(11) with amino acid and its derivatives were also studied [13-19].The literature survey reveals that very limited work of solid ternary complexes of transition metals with amino acids have been reported in the past [20-24].

EXPERIMENTAL SECTION

During the study analytical A.R. grade chemicals were used. An equimolar solution of proline and glycine or lysine 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 colored solid complexes were separated by slow evaporation. The formed solid complexes were recrystallized with double distilled water and dried in vacuum at70^{o}C.

RESULTS AND DISCUSSION

The elemental data presented in Table-1, are in good agreement with the stoichiometry [M(AB)] where,

M = Copper
A = Proline
B = Glycine & lysine

Thermal decomposition of complexes occurs in three stages. The first mass loss may be due to the loss of two water molecules in the chelates. The mass loss at a higher temperature indicates the elimination of ligands moiety. Above 380^{o}C the complexes begin to decompose, at first slowly and the increasingly rapidly, with the formation of CuO. The amounts of residue are in good agreement with the calculated values. The thermal decomposition data given in Table - 2.

Table 1: Elemental Data

S.No.	Mole. formula of complexes	Elemental Analysis								Color
		%C		%H		%N		%O		
		Obs	Cal	Obs	Cal	Obs	Cal	Obs	Cal	
1	Cu $C_7H_{12}O_4N_2.2H_2O$	35.12	36.43	6.32	5.34	7.31	8.21	28.68	29.44	Blue
2	Cu $C_{11}H_{20}O_4N_3.2H_2O$	32.06	32.40	5.39	4.60	8.14	8.32	34.40	35.3	Blue

Table 2: Thermal Analysis

S.No.	Complexes	Decomposition		Probable assignments
		Steps	Tem(0^oc)	
1	Cu $C_7H_{12}O_4N_2.2H_2O$	Ist	225	Loss of two water molecule
		IInd	278	Loss of one ligand moiety
		IIIrd	334	Loss of another ligand moiety
2	Cu $C_{11}H_{20}O_4N_3.2H_2O$	Ist	168	Loss of two water molecule
		IInd	233	Loss of one ligand moiety
		IIIrd	320	Loss of another ligand moiety

The visible spectrum data and magnetic moment are shown in Table-3. An asymmetric broad and weak band is observed at about 15,532 cm^{-1}, 16,169 cm^{-1} respectively for Cu $C_7H_{12}O_4N_2.2H_2O$ and $CuC_{11}H_{20}O_4N_3.2H_2O$. ϑ_{max} and extinction coefficient ε_{max} values indicate that the geometry of the complexes is tetragonally distorted octahedron[25]. The magnetic moment values are in the range 1.80 and 1.83 reported for the presence of one unpaired electron.

Table 3

S.N.	Complexes	Band Position cm^{-1}	ε $1mol^{-1}cm^{-1}$	μ
1	Cu $C_7H_{12}O_4N_2.2H_2O$	16,532 cm^{-1}	52.78	1.80
2	Cu $C_{11}H_{20}O_4N_3.2H_2O$	16,169 cm^{-1}	51.11	1.83

Table 4 shows the important IR band of the ligand and their complexes. The free amino acids proline, glycine and lysine exhibit $\vartheta(NH_2)$ in the range 3265-3300 cm^{-1}, $\vartheta_s(COO^-)$ an $\vartheta_{as}(COO^-)$ at 1450-1495 and 1630-1670 cm^{-1} respectively. For the mixed ligand complexes the stretching vibration of $\vartheta_s(COO^-)$ an $\vartheta_{as}(COO^-)$ appear in the range 1350-1405 cm^{-1} and 1575-1588 cm^{-1} respectively. It is to be moted that for both of the studied mixed amino acid complexes, $\vartheta_{as}(COO^-)$ appear as a band associated with a shoulder, indicating the presence of two different amino acids. The complexes further display a band in the range 3260-3280 cm^{-1} attributed to $\vartheta(NH_2)$, typical of coordinated amino group[26]. Metal nitrogen and metal-oxygen bonding are manifested by the appearance of two bands at 375-412 cm^{-1} and 450-495cm^{-1} respectively. The OH stretching vibrations of coordinate water are located in the range 3261-3193 cm^{-1}. No free carboxylic groups could be detected from the IR spectral data, indicating coordination of both of the studied metal ion to be the carboxylate anions.

From the given band positions, it may be concluded that the involved amino acids in the complexes are bidentate coordinating through the $-NH_2$ & -COOH groups[26].

Table 4: IR spectral data of the complexes cm^{-1}

S.N.	Complexes	$\vartheta_s(COO^-)$	$\vartheta_{as}(COO^-)$	$\vartheta(NH_2)$	$\vartheta(OH)_{H_2O)}$	ϑ(M-O)	ϑ(M-N)
1	Cu $C_7H_{12}O_4N_2.2H_2O$	1350	1575	3260	3261	450	375
2	Cu $C_{11}H_{20}O_4N_3.2H_2O$	1405	1588	3280	3193	495	412

The ESR spectra of the complexes shown in Table-5 indicates that complexes are paramagnetic in nature with one unpaired electron (d^9, magnetic moment 1.80-1.83 B.M.)

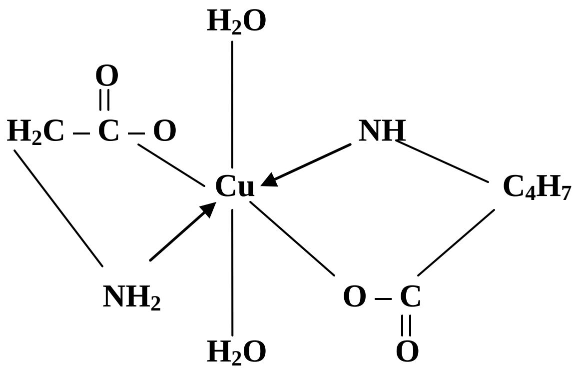
The trend $g_{11}>g_1>g_0$ observed suggest[27] the unpaired electron is localized in the $dx^2 - y^2$ orbital. The observed A_{11} and higher g_{11} values indicates[28] that there is slight distortion from planarity.

Table 5: ESR Spectral Parameters

S.N.	Complexes	ESR Parameters					
		g_t	g_e	g_{11}	g_1	A_{11}	A_1
1	Cu $C_7H_{12}O_4N_2.2H_2O$	2.1010	2.1152	2.1860	2.085	116	56.8
2	Cu $C_{11}H_{20}O_4N_3.2H_2O$	2.1214	2.1292	2.1917	2.040	114	50.3

The X-ray diffraction of pattern of the $CuC_7H_{12}O_4N_2.2H_2O$ indicates its high crystallinity. The diffractogram shows 14 reflections for 2θ value ranging from 11° to 54° with maxima at 2θ 17.12630° which corresponds to interplaner distance d 5.10564 A^O and λ value for is 4.4399 A^0.

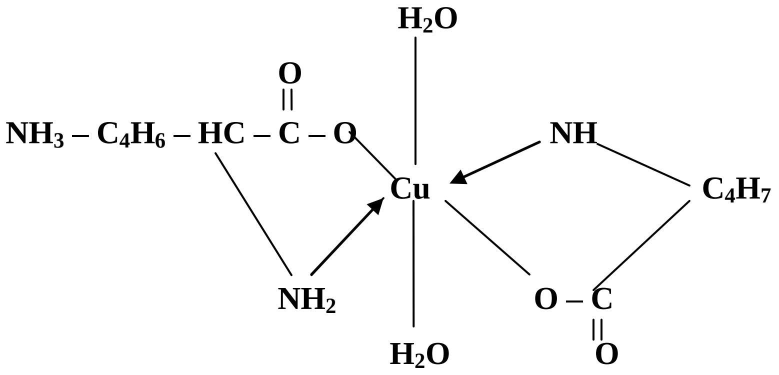
CONCLUSION



$Cu(C_7H_{12}O_4N_2)(H_2O)_2$

Figure 1

The results of elemental analysis suggest that the molecular formula of the complexes decomposition temp of the complexes indicate a strong metal-ligand bond visible and IR spectra studies suggest that Cu $C_7H_{12}O_4N_2.2H_2O$ and Cu $C_{11}H_{20}O_4N_3.2H_2O$ have distorted octahedral geometry and the symmetry of the complexes may be D4h. in the terms of above study we can represent the structure of complexes as shown below in Fig.1 & Fig.2.



$Cu(C_{11}H_{20}O_4N_3)\ (H_2O)_2$

Figure 2

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