



Spectroscopic and thermal studies of copper (II) complexes with different amino acid

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ABSTRACT

Ternary complexes of Copper (II) with different amino acids have been prepared, in which proline taken as a common ligand and valine or threonine taken as secondary ligand. Amino acids have the tendency to form complexes with different metals and have important significance in biological and pharmaceutical fields. The complexes have been characterized by elemental analysis, magnetic measurement, thermal analysis, ESR, IR, XRD spectral studies. A distorted octahedral structure has been proposed for all the prepared complexes.

Key words: Ternary complexes, ligand, amino acids, spectroscopic studies, distorted octahedral structure.

INTRODUCTION

Mixed ligand complexes play a vital role in biological process [1-2]. The stabilities of mixed ligand complexes show great importance in biological and toxicological functions are directly or indirectly dependent on stability of complexes. Most of the physiological activities are promoted by metal ions through the formation of mixed ligand complexes[3-9]. Still the mixed ligand complexes of amino acids continue to be an important field of study because they are incorporated in biochemical structures, such as cytochromes of mitochondrial membranes, hemoglobin and chlorophyll and have been of great interest due to their importance as biological active agent [10-12]. Some Copper (II) mixed ligand complexes are found to exhibit a variety of pharmacological activity and superoxide dismutase activity⁽¹³⁾. In mixed ligand complexes carboxylate ligands play an important role in supramolecular assembly owing to versatile co-ordination modes of the carboxyl group [14-19]. Many attempts have been made to correlate the stability of the metal ligand complexes with their antimicrobial activity [20-25]. In Copper (II) amino acid complexes, Copper (II) ion has preferred square planar geometry; therefore it binds a maximum of two amino acids. This provides the possibility for mixed Copper (II) amino acid co-ordination to occur which has been demonstrated under physiological condition [26], as well as in vitro system [27-30].

EXPERIMENTAL SECTION

During the study analytical A.R. grade chemicals were used. An equimolar solution of proline and valine or threonine 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 at 70°C.

RESULTS AND DISCUSSION

The analytical data presented in **Table 1**, are in good agreement with the stoichiometry [Cu (AB)] where A is proline & B is valine or threonine.

The DTA curves show three stage decomposition. The important decomposition stage is observed at 325^oC, 300^oC respectively for [Cu (Pro)(Val) (H₂O)₂] and [Cu(Pro)(Threo) (H₂O)₂] afterwards the process of oxidation of inorganic substance begins, and it has been observed that along with decomposition oxidation of organic substance also takes place. The final black product is CuO. Water molecules eliminated at around 175^oC may be coordinated water [31].

TABLE – 1 Physico-chemical data of the Complexes

| S. N. | Complexes | Decomp. | | Elemental Analysis | | | | | | | |
|-------|--|---------|-------------|--------------------|-------|------|------|------|------|-------|------|
| | | Stage | Temp. °C | % C | | % H | | % N | | % O | |
| | | | | Obs. | Cal. | Obs. | Cal. | Obs. | Cal. | Obs. | Cal. |
| 1. | Cu(C ₁₀ H ₂₀ N ₂ O ₄) ₂ H ₂ O | I | 200 | 35.02 | 36.47 | 5.33 | 5.47 | 7.61 | 8.51 | 27.98 | 29.8 |
| | | II | 250 | | | | | | | | |
| | | III | 325 | | | | | | | | |
| 2. | Cu(C ₉ H ₁₈ N ₂ O ₄) ₂ H ₂ O | I | 178 | 31.06 | 32.40 | 4.39 | 4.80 | 8.27 | 8.40 | 33.40 | 35.5 |
| | | II | 220 | | | | | | | | |
| | | III | 300 | | | | | | | | |

The visible spectrum data is shown in **Table 2**. An asymmetric broad and weak band is observed at about 16,129 cm⁻¹, 16,666 cm⁻¹ respectively for [Cu(Pro)(Val) (H₂O)₂] and [Cu(Pro)(Threo) (H₂O)₂]. λ_{\max} and extinction coefficient ϵ_{\max} values indicate that the geometry of the complex is tetragonally distorted octahedron [32]. This complex may be assumed to be trans isomer[33] with D_{2h} symmetry based on the appearance of only one band. The symmetry of the complex may be assumed to be D_{4h} in which N-atoms are taken equivalent to O- atoms. The change in concentration of the solution does not alter the value of λ_{\max} , hence the complex does not undergo dissociation or association.

TABLE – 2 Electronic Spectral Data of the Complexes

| S. N. | Complexes | λ_{\max} (nm) | ABS | Wave number (cm ⁻¹) | Energy (ev) | Frequency (THz) | ϵ_{\max} (mol ⁻¹ cm ⁻¹) |
|-------|--|-----------------------|-------|---------------------------------|-------------|-----------------|---|
| 1. | Cu(C ₁₀ H ₂₀ N ₂ O ₄) ₂ H ₂ O | 620 | 0.212 | 16,129 | 2.00 | 483 | 51.45 |
| 2. | Cu(C ₉ H ₁₈ N ₂ O ₄) ₂ H ₂ O | 615 | 0.199 | 16,666 | 2.07 | 499 | 53.07 |

IR spectra and band assignment of the Copper (II) complexes are given in **Table-3**. For the mixed ligand complexes the stretching vibration of ν_s (COO⁻) and ν_{as} (COO⁻) appear in the range 1365-1480 cm⁻¹ and 1532-1685 cm⁻¹. ν_{as} (COO⁻) band indicate the presence of two different amino acids. The coordination of nitrogen atom of the -NH₂ with metal ion is indicated by the shift of -NH band to 3198 cm⁻¹ – 3270 cm⁻¹ typical of coordinated amino group[34]. In the far IR spectra ν (M-O) and ν (M-N) stretching vibration modes appear in the ranges 455-480 cm⁻¹ and 368-390cm⁻¹, respectively. The range 3200-3395 cm⁻¹ indicates the OH stretching vibration of coordination water. Free carboxylic 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 -NH₂ and COO⁻ groups.

Table – 3 IR Spectral data of the complexes (cm⁻¹)

| S.N. | Complexes | ν_s (COO ⁻) | ν_{as} (COO ⁻) | ν (NH ₂) | ν (OH) | ν (M-O) | ν (M-N) |
|------|--|-----------------------------|--------------------------------|--------------------------|------------|-------------|-------------|
| 1 | Cu(C ₁₀ H ₂₀ N ₂ O ₄) ₂ H ₂ O | 1365 | 1532 | 3198 | 3395 | 455 | 368 |
| 2 | Cu(C ₉ H ₁₈ N ₂ O ₄) ₂ H ₂ O | 1480 | 1685 | 3270 | 3200 | 480 | 390 |

Table – 4 ESR DATA

| S.N. | Complexes | ESR Parameters | | | | | | μ eff(BM) |
|------|--|----------------|--------|----------|-------|----------|-------|---------------|
| | | g_1 | g_e | g_{11} | g_1 | A_{11} | A_1 | |
| 1 | Cu(C ₁₀ H ₂₀ N ₂ O ₄) ₂ H ₂ O | 2.1229 | 2.1264 | 2.1760 | 2.060 | 117 | 54.5 | 1.83 |
| 2 | Cu(C ₉ H ₁₈ N ₂ O ₄) ₂ H ₂ O | 2.1231 | 2.1253 | 2.1780 | 2.085 | 122 | 50.6 | 1.84 |

The ESR spectra of the complexes shown in **Table-4** indicate that complexes are paramagnetic in nature with one unpaired electron (d⁹, magnetic moment 1.83-1.84BM).The trend $g_{11} > g_1 > g_0$ observed suggests[35] the unpaired

electron is localized in the $d_{x^2-y^2}$ orbital. The observed A_{11} and higher g_{11} values indicates [36] that there is slight distortion from planarity.

The x-ray diffraction data of [Cu (Pro) (Val) (H₂O)₂] complex shows in **Table – 5**. The x-ray diffraction pattern of the [Cu (Pro)(Val) (H₂O)₂] indicates its high crystallinity. The diffractogram at $2\theta = 17.6009^\circ$ which corresponds to interplaner distance $d = 5.03485 \text{ \AA}$. The λ value for this peak is 2.9404 \AA . The unit cell parameters were calculated from indexed data. It is also clear from the data that Cu (II) complex has cubic symmetry.

TABLE – 5 Crystal parameter

| S. N. | Complex | Lattice const. | λ (Å ⁰) | n | Density gm/cm ³ | Crystal system | Rel. ref. |
|-------|--|----------------|-----------------------------|---|----------------------------|----------------|-----------|
| 1. | Cu(C ₁₀ H ₂₀ N ₂ O ₄) ₂ H ₂ O | 2.9068 | 2.9404 | 4 | 7.5167×10^{-22} | Cubic | 14 |

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_{4h}. 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. From the XRD studies this may confirm the formation of the mixed ligand complexes and indicates the presence of a mixture of two binary complexes.

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