

Synthesis, Characterization and Antimicrobial Activity of Mixed-Ligand Complexes of Cu(II) with 1,2,4, Triazole and Amino Acids

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Abstract

Mixed-ligand ternary complexes of Cu (II) metal ion with 1,2,4 triazole (TRZ) and amino acids (histidine (L¹), threonine (L²), proline (L³) and hydroxyl proline (L⁴)) have been synthesized. The prepared ternary chelates were characterized by elemental analysis, IR and electronic spectra, as well as conductivity measurements. The general formula [Cu(TRZ)L]H₂O were found for the ternary chelates containing TRZ. From the analytical and spectral data, the stoichiometry has been found to be 1:1:1 for all the complexes. A tetrahedral geometry has been proposed. Molecular modeling studies were also carried out to confirm the geometries of the complexes. All the new complexes were found to be active against bacteria.

Keywords: Triazole; Amino acids; Microbial activity; Ternary complexes.

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1. Introduction

Triazoles and their derivatives constitute an interesting class of heterocyclics which gained considerable attention in recent years because 1,2,4 triazole (TRZ) represents a hybrid of pyrazole and imidazole with regards to the arrangement of ring nitrogens. The importance of triazole compounds and their metal complexes in the biological fields is well recognized in the literature [1-8]. The bioactivities of such compounds have been correlated to their complexing ability with metal ions [9]. Therefore, a considerable amount of work on binary metal complexes of triazole compounds has been reported [10-24]. Co(II), Ni(II) and Cu(II) complexes of TRZ and 3-mercapto TRZ with dicarboxylic amino acids [aspartic acid and glutamic acid] and their characterization were reported [25]. This widespread interest is based on several important properties of the triazoles. Because of the position of the donor atoms in the five-membered ring, the triazoles appear

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to possess the possibility of linking (transition) metal ions together. The triazole ligands thereby constitute a bridge between the metal ions. This bridge can be of several geometries, depending on the donor atoms of the ligand and the properties of the metal.

In nature, many metallo proteins appear to have active sites comprising pairs of metal ions in close proximity. Much research is also devoted to mimicking these enzymatic reactions by functionalized models or using such complexes in reactions other than the enzymatic ones. The fact that TRZ's are quite similar in geometry to imidazoles, which occur overwhelmingly in nature, is a second property that has made the triazoles and triazole complexes much sought after compounds to mimic natural processes. They are also used to mimic imidazoles in model compounds for such processes. The TRZs are being widely used as pharmaceuticals and as agricultural chemicals and this may be connected to this similarity in geometry as well as coordinative properties.

Moreover no attempts have been made to prepare ternary metal complexes of Cu(II) with the ligands TRZ and histidine, threonine, proline and hydroxy proline. The characterization of the prepared ternary chelates was achieved by elemental analysis, molar conductance, infrared, electronic and mass spectral measurements.

2. Experimental

2.1. Materials and methods

The metal salt ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$), TRZ and amino acids [histidine, threonine, proline and hydroxy proline] from Aldrich or Merck were of analytical grade. All other chemicals used were also of analytical grade. Elemental analysis (C, H, N) of the ternary metal complexes was carried out using a Perkin-Elmer 240CSA elemental analyzer. Molar conductances of the metal complexes were measured in DMSO solution using Digisun digital conductivity meter. Magnetic susceptibilities of the complexes were measured on Guoy balance, model 7550 using $\text{Hg}[\text{Co}(\text{NCS})_4]$ as standard. The diamagnetic corrections of the complexes were done using pascal's constants. Melting points of the ligands and m.p./decomposition temperature of complexes were determined on Polmon instrument (MP-96). IR spectra were recorded in KBr discs on Bruker FT-IR Spectrometer from 400 to 4000 cm^{-1} . Electronic spectra were recorded with Elico SL 159 UV-visible Spectrophotometer. Molecular mechanics calculations were done with Argus lab software, an interactive graphics program.

2.2. Molecular modeling studies

Molecular mechanics calculations were done with Argus lab software [26] an interactive graphics program that allows rapid structure building, geometry optimization and molecular display. Molecular modelling software Argus lab has the ability to handle transition metal complexes. Energy minimization was repeated several times to find global minimum. [26-32].

2.3. Synthesis of ternary metal complexes

The following general procedure has been adopted for the synthesis of the ternary complexes. The copper nitrate salt (5 mmol) (1.205 g) dissolved in a minimum quantity of water was added slowly to ethanol (10 mL) solution of the triazole [TRZ (0.345 g)] with stirring. A 10 mL of an EtOH solution (5 mmol) of the amino acid [histidine (0.775), threonine (0.595), proline (0.576) and hydroxy proline (0.655)] was then added dropwise to the above mixture with continuous stirring. The solutions of the ternary mixtures were neutralized using an aqueous solution of 0.1 mol dm^{-3} KOH. The ternary mixture was refluxed for 5 h and then evaporated to small volume and left to cool. The solid ternary complexes were precipitated out. The solid complexes were filtered and washed thoroughly with H_2O and EtOH and dried over CaCl_2 .

3. Results and Discussions

3.1. Physical character

The elemental analysis data along with some physical properties of the synthesized ternary complexes are given in Table 1. The formation of the ternary metal complexes may be represented by the Eq. (1) for the complexes containing TRZ. The Prepared ternary complexes are insoluble in water as well as in most common organic solvents. However, they are slightly soluble in DMF and DMSO.

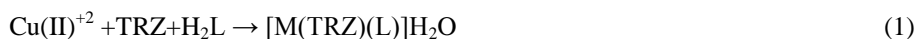


Table 1. Analytical data and physical properties of the different synthesized ternary complexes.

Complex	Molecular formula	M.Wt	M.P. °C	C%	H%	N%	Molar conduct. ($\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$)
$[\text{Cu}(\text{TRZ})\text{L}^1\text{Cl}]\text{H}_2\text{O}$	$\text{CuC}_8\text{H}_{11}\text{N}_6\text{O}_2\text{Cl}$	332	249	29.8	3.41	26.0	11.9
$[\text{Cu}(\text{TRZ})\text{L}^2]\text{H}_2\text{O}$	$\text{CuC}_6\text{H}_{10}\text{N}_4\text{O}_3$	250	223	28.85	4.0	22.0	13.3
$[\text{Cu}(\text{TRZ})\text{L}^3\text{Cl}]\text{H}_2\text{O}$	$\text{CuC}_7\text{H}_{11}\text{N}_4\text{O}_2\text{Cl}$	282	260	29.2	3.83	19.5	15.2
$[\text{Cu}(\text{TRZ})\text{L}^4]\text{H}_2\text{O}$	$\text{CuC}_7\text{H}_8\text{N}_4\text{O}_3$	258	272	32	3.08	21.5	12.5

Molar conductance

The measured molar conductance values of $10^{-3} \text{ mol dm}^{-3}$ DMSO solutions of the ternary complexes are in the range $10\text{-}15 \text{ ohm}^{-1}\text{cm}^2 \text{mol}^{-1}$ L, indicating the non-electrolytic nature of these complexes [33].

Thermo Gravimetric Analysis

Generally, two types of water molecules are associated with the complexes viz, lattice water and coordinated water. The lattice water lost at lower temperature ($60\text{-}120^\circ\text{C}$)

where as the coordinated water molecule lost at higher temperatures (150-200°C) [34]. A small weight loss in the range of 80-100°C is assigned to the loss of lattice water. Maximum and gradual weight loss in the range of 360-1000°C is attributable to the decomposition of ligand moiety. The residue at 1000°C indicates the non-volatile metal component present in the complex (Fig. 1).

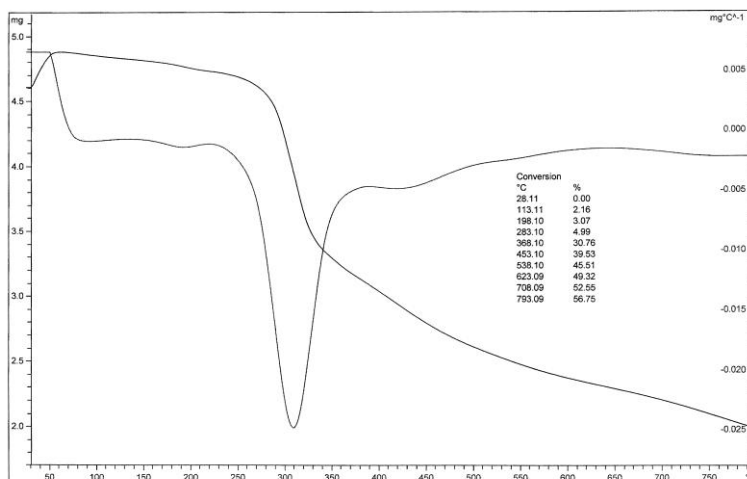


Fig.1. Thermogram of $\text{Cu}(\text{TRZ})\text{L}^4\text{H}_2\text{O}$ complex.

3.3. IR spectra

The most important IR bands of prepared ternary complexes providing conclusive evidence for the coordination mode are presented in Table 2. The free triazole ligands display a strong band in the range $3138\text{-}3140\text{ cm}^{-1}$, which is ascribed to the stretching vibration of N-H of the pyrrolic nitrogen atom. However, this band shows no significant change in the IR spectra of the various isolated ternary complexes. The stretching vibration of the azomethine (C=N) group appearing in the range of $1518\text{-}1520\text{ cm}^{-1}$ in IR spectra of triazole ligand [17] are shifted to lower frequencies in the ternary complexes, suggesting the involvement of this group in the coordination. This is consistent with the formation of a coordinative bond between the nitrogen atom of the heterocyclic ring and the metal cation. This may be substantiated by a similar conclusion reached previously for similar ligands [17, 35, 36].

On the other hand, the presence of hydrated or/and coordinated water molecules in the prepared ternary complexes is verified by the presence of broad or shoulder bands in the high frequency region at $3550\text{-}3300\text{ cm}^{-1}$ in the IR spectra, attributed to the OH vibration of water (Table 2). Further, the appearance of a strong band in the $893\text{-}895\text{ cm}^{-1}$ region, is assignable to the OH rocking vibration.

Table 2. Infrared spectral data (cm⁻¹) of the mixed-ligand ternary complexes.

Complexes	V _{OH/H₂O}	V _{NH₂}	V _{NH}	V _{asym⁻COO⁻}	V _{C=N}	Sym V _{coo⁻}	V _{rocking mode(OH)}
[Cu(TRZ)L ¹]H ₂ O	3418	2918	3138	1628	1508	1385	895
[Cu(TRZ)L ²]H ₂ O	3427		3140	1633	1502	1385	893
[Cu(TRZ)L ³]H ₂ O	3420		3140	1633	1505	1385	893
[Cu(TRZ)L ⁴]H ₂ O	3420		3140	1633	1503	1385	895

A distinct band appearing in the 1628-1633 cm⁻¹ region in the IR spectra of various complexes is typical of the stretching vibration of a coordinated COO⁻ group. This assignment is based on the stretching vibration band of non ionized and non coordinated COO⁻ appearing in the 1750-1700 cm⁻¹ region, whereas that of the ionized and coordinated COO⁻ occurs in the 1650-1590 cm⁻¹ range [37]. The amino acid ligands are coordinated to the metal ion as divalent anions via the oxygen atom of the carboxylate groups. Further, the observed weak band at 1385 cm⁻¹ in the IR spectra is responsible for the symmetric vibration frequency of the coordinated COO⁻ group [37] and is further evidence for the participation of the carboxylate group in the coordination with the central metal ion. However, in some cases this band overlaps with the symmetric vibration of the C=N group in the triazole moiety and appears as one broad band in the IR spectra. In L², L³ and L⁴ complexes this band is disappeared. This change is consistent with the contribution of this group in the coordination to the central metal ion.

In free histidine, imidazole nitrogen stretching frequency at 962 cm⁻¹ shifted to higher frequency at 1039 cm⁻¹, indicates involvement of imidazole nitrogen in coordination with metal ion. In threonine, hydroxyl proline complexes the broad peak of OH disappeared, this indicates OH is involved in coordination with metal. In complexes of proline, hydroxyl proline NH stretching frequency is shifted to high, indicating that group is involved in coordination with metal ion. The stretching vibration band of the NH₂ group in the free aminoacid (threonine) centered at the vicinity of 3183cm⁻¹, disappeared in the IR spectrum of the ternary complex. This change indicates that this group is in coordination with of threonine anion to the central metal ion. The stretching vibration band of the NH₂ group in the free aminoacid (histidine) centered at the vicinity of 2918cm⁻¹, appeared in the IR spectrum of the ternary complex. This indicates that this group is not in coordination with the central metal ion.

Thus, one may conclude that the amino acids are chelated to the central metal ion as anionic tridentate O,O,N ligands via the oxygen atoms of the carboxylate groups and the nitrogen atom of the NH₂ group and oxygen atom of the OH group. On the other hand, the ligand TRZ is coordinated to the metal ion as a neutral monodentate through the heterocyclic nitrogen atom. One such IR spectra of [Cu(TRZ)L⁴]H₂O complex is illustrated in Fig. 2.

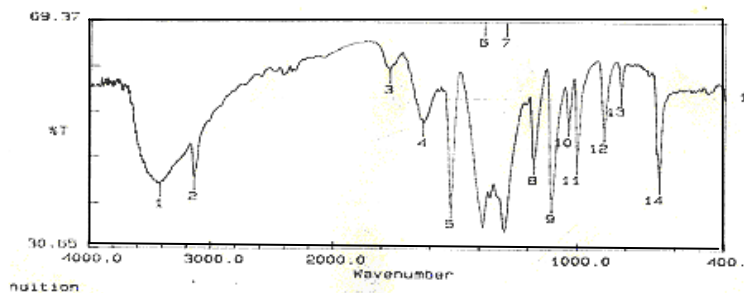


Fig. 2. IR Spectrum of $[\text{Cu}(\text{TRZ})\text{L}^4]\text{H}_2\text{O}$ complex.

3.4. Electronic spectra and magnetic moment susceptibility measurements

The electronic absorption (UV–VIS) spectra of metal complexes were recorded in DMSO, in the range of 200–1100 nm and the data is listed in Table 3. The magnetic moment data and the proposed geometry of the complexes are also presented in the same table. These values are closer to those reported in some similar type of complexes [37].

The electronic spectra of Cu(II) ternary complexes containing the TRZ moiety display absorption band in the range 420–485 nm. This band is ascribed to the intramolecular (ligand→M) charge transfer transition.

Table 3. Electronic absorption spectra and magnetic moment data of complexes.

Complex	λ_{nm}	Band assignment	Mag. moment (μ_{eff}) B.M	Geometry
$[\text{Cu}(\text{TRZ})\text{L}^1]\text{H}_2\text{O}$	670	${}^2\text{B}_{2g} \rightarrow {}^2\text{E}_{1g}$ and ${}^2\text{B}_{2g} \rightarrow {}^2\text{A}_{1g}$	1.73	Tetrahedral
	418	ligand→M CT transition		
$[\text{Cu}(\text{TRZ})\text{L}^2]\text{H}_2\text{O}$	685	${}^2\text{B}_{2g} \rightarrow {}^2\text{E}_{1g}$ and ${}^2\text{B}_{2g} \rightarrow {}^2\text{A}_{1g}$	1.68	Tetrahedral
	445	ligand→M CT transition		
$[\text{Cu}(\text{TRZ})\text{L}^3]\text{H}_2\text{O}$	660	${}^2\text{B}_{2g} \rightarrow {}^2\text{E}_{1g}$ and ${}^2\text{B}_{2g} \rightarrow {}^2\text{A}_{1g}$	1.88	Tetrahedral
	435	ligand→M CT transition		
$[\text{Cu}(\text{TRZ})\text{L}^4]\text{H}_2\text{O}$	690	${}^2\text{B}_{2g} \rightarrow {}^2\text{E}_{1g}$ and ${}^2\text{B}_{2g} \rightarrow {}^2\text{A}_1$	1.72	Tetrahedral
	430	ligand→M CT transition		

In addition to the above transitions, the electronic absorption spectra of the ternary complexes display a main absorption band at 660–690 nm for the complexes containing the amino acids. It was reported previously that four-coordinate Cu(II) complexes have d-d transitions at about 1112–1250, 699–917 or 699–917 nm for regular tetrahedral, pseudo-tetrahedral or square-planar structure has been suggested for Cu(II) complexes having a d-d transition band around 610 nm [38–40], a pseudo-tetrahedral or square planar structure was also suggested for Cu(II) complexes with a maximum absorption in the 610–625 nm range [40,41]. Considering the above fact that the absorption maximum related to four

coordinate Cu(II) complexes shifts to higher energy as the regular tetrahedral structure is distorted towards a square planar one [42], one can suggest a pseudo-tetrahedral structure for the present four coordinate Cu(II) complexes. Thus, the recorded band in the 660-690 nm region for synthesized ternary complexes in the present study can be attributed to the ${}^2B_{2g} \rightarrow {}^2E_{1g}$ and ${}^2B_{2g} \rightarrow {}^2A_{1g}$ transitions [42].

3.5. Antimicrobial activity

The antibacterial activity of the ligands and its Cu(II) complexes have been studied against *E.coli* and *Staphylococcus aureus* by paper disc method. The concentration of each sample was maintained at 200 $\mu\text{g/mL}$, 100 $\mu\text{g/mL}$ and 50 $\mu\text{g/mL}$ in DMSO respectively. In the present study, the zones of inhibition of antibacterial activity have been presented in Table 4. The results indicate that the complexes show highest activity against *E.coli* and *S.aureus* at 20 $\mu\text{g/mL}$ and 100 $\mu\text{g/mL}$ respectively. The mode of action of the compounds may involve in formation of a hydrogen bond through the azomethine group with the active centres of cell constituents, resulting in an interference with the normal functioning of the cell [43].

The results of the complexes are presented in Table 4 and Fig. 3. The data presented in the Table also reveal that antibacterial activities of $[\text{Cu}(\text{TRZ})\text{L}^3]\text{H}_2\text{O}$, $[\text{Cu}(\text{TRZ})\text{L}^4]\text{H}_2\text{O}$ metal complexes are relatively high.

Table 4. Antimicrobial activity of Cu(II) ternary metal complexes (growth inhibition zones of microbes in mm).

Complex	E.Coli	Staph	E.Coli	Staph	E.Coli	Staph
	200 $\mu\text{g/ml}$	200 $\mu\text{g/ml}$	100 $\mu\text{g/ml}$	100 $\mu\text{g/ml}$	50 $\mu\text{g/ml}$	50 $\mu\text{g/ml}$
$[\text{Cu}(\text{TRZ})\text{L}^1]\text{H}_2\text{O}$	7	8	5	7	---	---
$[\text{Cu}(\text{TRZ})\text{L}^2]\text{H}_2\text{O}$	8	9	4	7	2	2
$[\text{Cu}(\text{TRZ})\text{L}^3]\text{H}_2\text{O}$	10	7	6	5	2	3
$[\text{Cu}(\text{TRZ})\text{L}^4]\text{H}_2\text{O}$	9	8	7	8	4	2
DMSO Control	---	---	---	---	---	---

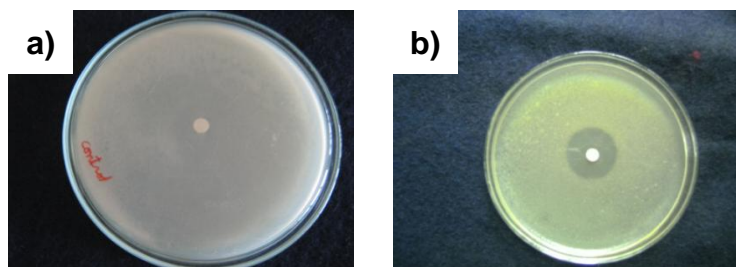
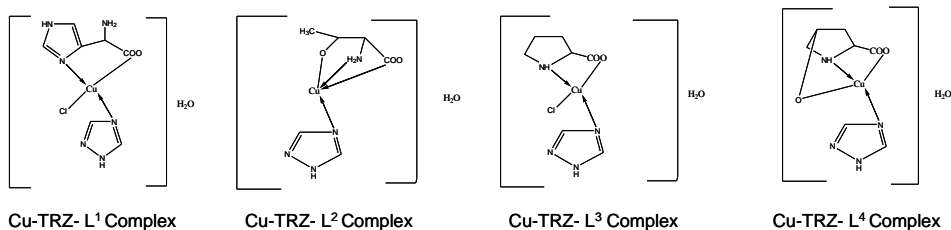


Fig. 3. a) DMSO control and b) inhibition zone of $[\text{Cu}(\text{TRZ})\text{L}^3]\text{H}_2\text{O}$.

3.6. Proposed structures of metal complexes



3.7. Molecular modeling structures

The possible geometries of metal complexes were evaluated using the molecular calculation with Argus lab software. The geometrical optimization of the structures obtained is presented in Fig. 4.

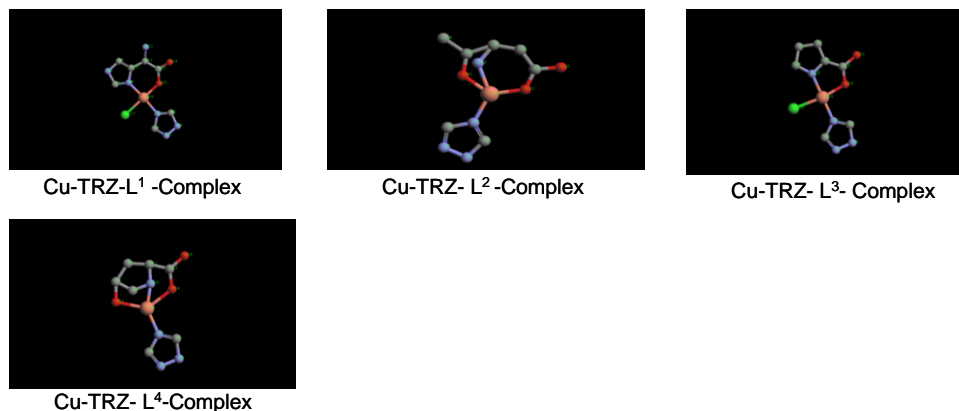


Fig. 4. Geometries of mixed-ligand ternary complexes.

4. Conclusions

Mixed-ligand ternary complexes of Cu(II) metal ion with TRZ and amino acids have been synthesized. The prepared ternary chelates were characterized by elemental analysis, IR and electronic spectra, as well as conductivity measurements. All the complexes are non-electrolytes in DMSO. The general formula $[\text{Cu}(\text{TRZ})\text{L}]\text{H}_2\text{O}$ were found for the ternary chelates containing TRZ. From the analytical and spectral data, the stoichiometry has been found to be 1:1:1 for all the complexes. Based on analytical, molar conductance, magnetic and spectral data a tetrahedral geometry has been proposed. Molecular modeling studies were also carried out to confirm the geometries of the complexes. All the new complexes were found to be active against bacteria.

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