



Synthesis, Spectral and Electrochemical analysis of Copper(II) complexes with L-threonine, L-tyrosine, L-tryptophane and L-histidine

KEYWORDS

copper(II), aromatic amino acids, IR, UV and CV

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ABSTRACT Copper α -amino acid complex attracts attention of chemists because of its different kind of biological applications. Amino acids having both, amine and carboxylic acid groups attached to the first, or alpha, carbon atom have particular importance in biochemistry. Complexes of copper(II) with amino acids can be used as models to study the pharmacodynamic effects of drugs or for increasing the biocompatibility and minimize toxic effects of some metal ions. Therefore, this attraction we were synthesized the new series of complexes of copper(II) with various amino acids namely L-threonine, L-tyrosine, L-tryptophane, L-histidine and characterized as mononuclear species on the basis of elemental chemical analysis, infrared spectra, UV-Visible and cyclic voltametry measurements. The IR spectra indicated the presence of amino acid coordinated through nitrogen atom and the oxygen from the carboxylic group. The experimental data suggest that the ligands act as bidentate and adopt an octahedral stereochemistry. This paper consist synthesis, elemental analysis and characterization of these complexes.

Introduction

The development of modern chemotherapy is based on metals and metal complexes which play a key role in modifying the pharmacological properties of known drugs after coordinating to a metal. Many metal ions are known to play very important roles in biological processes in the human body (Kaim et al 1996 and Xiao-Ming et al 1996). Cu(II) complexes are interesting due to their biological applications and considerable amount of interest in the studies is due to their coordination modes when bound to metals, high pharmacological potentiality and good chelating property. Cu(II) is a bio-essential element occurring in multitude of metalloproteins (Bhattacharjee et al 2010). Complexes of Cu(II) with amino acids can be used as models to study the pharmacodynamic effects of drugs or for increasing the biocompatibility and minimize toxic effects of some metal ions (Greco et al 1986 and Asmal et al 2001). Metallotherapy is a very unique therapeutic method to treat many diseases. Several metal ions and their complexes exhibit anti-diabetic effects (Schwarz et al 1959, Rubenstein et al 1962, Coulston et al 1980, Heyliger et al 1985, Sakurai et al 1990 and Yoshikawa et al 2000). It appears attractive to many researchers to study the relationship between diabetes mellitus and metal ions. Therefore, this attraction we were synthesized the new Cu(II) complexes containing L-threonine, L-tyrosine, L-tryptophane, L-histidine as ligands. In this paper there is an increased focus on studies carried out on the complexation of Cu(II) with amino acids. The synthesized complexes were characterized by elemental analysis, CV, IR, UV-visible.

Experimental**Materials and Methods**

Chemicals: Triple distilled water, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$, CuCl_2 , sodium acetate were purchased from alfa aesar, Great Britain. All solvent were HPLC grade and used further purification.

Synthesis of complexes: The $[\text{Cu}(\text{L})_2]^{+2}$ complexes were prepared from three different salts of copper and amino

acids (L-threonine, L-tyrosine, L-tryptophane, L-histidine) as ligand. 2 mM of amino acid was added in 20 ml of aqueous solution which containing 2 mM of sodium acetate and allow it to a clear solution with continuous string. Then 1 mM of metal salt in 2 ml of triple distilled water was added drop by drop into this aqueous solution with continuous string for 3 hours. A deep blue colored solution obtained which were transferred into petri dish for crystallization. After few days deep blue colored crystals obtained.

Infrared spectroscopy: Infrared (IR) spectra were obtained by the KBr method using a Bruker Alfa-T model Fourier transform (FTIR) spectrometer (Bruker Instrument Germany). The spectrometer was equipped with a Globler IR source, KBr beam splitter and detector. For each spectrum, 16 scans were obtained with the resolution of 4 cm^{-1} . The obtained IR spectra were proceed by mean of the program OPUS 7.0.

UV-VIS spectroscopy: The UV-visible transmittance spectra of the complexes were recorded at 25°C on a Shimadzu UV-Vis 160 spectrophotometer, in quartz cells at the desired wave length region. 3 mM solution of complexes in DMSO was used in all UV-visible measurements.

Cyclic voltametry: The cyclic voltametric measurements were carried out with a Metrohm Instrument (Germany) having an electrochemical cell with a three-electrode system. The reference electrode was an Ag/AgCl_2 . Platinum wire used as a working electrode, Platinum wire electrode used as an auxiliary electrode. The 3 mg of complex were dissolved in supporting electrolyte 25 ml of 0.01 M solution of KCl solution. The voltamogram, peak position and area were calculated using NOVA 1.9 software.

Results and Discussion:**Characterization of metal complexes**

All the complexes are colored, non-hygroscopic and thermally stable solids. Elemental data of the complexes were given in Table-1. The complexes are insoluble in common

organic solvents such as ethyl alcohol, acetone, etc., but are fairly soluble in H₂O and DMSO.

Table(1) : Elemental analysis data of copper complexes with amino acids.

SN	Complex	Empirical formula	Molecular weight	Color	Elemental analysis Found			
					M %	C %	H %	N%
1.	[Cu(thr) ₂](SO ₄) ₂	C ₄ H ₁₀ N ₂ O ₄ Cu	301.5	Shining dark blue	21.06	31.85	5.97	9.28
2.	[Cu(tyr) ₂]Cl ₂	C ₁₀ H ₂₂ N ₂ O ₄ Cu	413.5	Royal blue	15.35	52.23	5.32	6.77
3.	[Cu(trp) ₂](NO ₃) ₂	C ₈ H ₂₈ N ₄ O ₆ Cu	471.5	Dark blue	12.78	55.99	5.09	11.87
4.	[Cu(his) ₂](CH ₃ COO) ₂	C ₁₂ H ₂₈ N ₈ O ₄ Cu	373.5	brown	17.03	38.55	4.81	22.48

Infra Red spectroscopy:

Infrared studies on coordination compounds of amino acids have shown that the coordination of metal with ligand, making it a useful tool in structural studies (Nakamoto et al 2009). In the IR spectrum of complex(3), [Cu(trp)₂] the spectra exhibited a marked difference between bands belonging to the stretching vibration of ν(N-H) of the amine group in the range between 3469-3382cm⁻¹ shifted to higher frequencies by 92-27 cm⁻¹ suggesting the possibility of the coordination of ligand through the nitrogen atom at the amine group (Nakamoto et al 1967, Maracotrigiano et al 1975, Kothar et al 1996). In order to get further information about the coordination behavior of the ligand with metal ion, the N-H stretching vibration at 3119 cm⁻¹ in the complex was shifted to higher frequencies with the complexes, suggesting that the coordination of the metal ions with the ligand was via the nitrogen atom (Fessenden 1990, Nakamoto et al 2009 and Elzahany et al 2008). The infrared spectra of the complex(1) is given in Fig-1. The absorption band at 1624 cm⁻¹ was attributed to the ν(C=O) stretching vibration in the spectrum. The consecutive bands at 1600 and 1572 cm⁻¹, in the spectrum of the ligand were assigned to the symmetric and asymmetric bending vibrations of N-H bond. The complexes 1, 2, 3 and 4 spectra, which involves the carboxylic group in the covalent bonding to the metal ion (David et al 2003). In the spectrum of the complexes are shifted to 1578 cm⁻¹ and 1584 cm⁻¹, which also indicates the involvement of this group in the metal-ligand bond formation. The important absorption at assignment of the complex 1, 2, 3 and 4 are listed in Table-2.

UV-VIS spectroscopy:

The electronic spectra data of the complexes were recorded in 100% DMSO and their assignments were given in Table-3 and one representative ligand field spectra of complex(1) [Cu(thr)₂] is shown in Fig.-2 and band position are presented in Table- 3. The UV-Vis spectra of Cu(II) complexes with the four ligands show absorption bands assigned to a large band around 620 nm (16000 cm⁻¹). The presence of the later band supports an octahedral stereochemistry for these complexes (Miessler et al 1999). Two bands were observed in the electronic spectrum of the complex(3), at 631 nm and 819 nm which can be assigned to ²B_{1g} → ²B_{2g} and ²B_{1g} → ²E_g transitions (Miessler et al 1999). Characteristic π-π* transitions are observed in the spectrum at 233, 235, 247, 256 nm respectively (Eskander et al 2000 and Reddy et al 2000).

Electrochemical studies of complexes:

Figure- 4 shows cyclic voltammogram (CV) scanned cathodically in the potential region between +0.00 and -0.750 V vs Ag/AgCl in 0.1M sodium perchlorate solution [CuL₂]²⁺ systems at different pH (isoelectric point of amino

acids). In this scan range, the CVs show a single reduction peak at -498.03 mV (A1) in the forward sweep only one oxidation waves (B1) at 24.63 mV/s at the scan rate of 0.01 V/s. Voltammogram clearly represents that reduced moiety of Cu(II) doesn't fully oxidized in further sweep.

Table-2 : max (nm) values (in 100% DMSO solution) for Copper(II) complexes.

SN	Complex	λ _{max} (nm)
1	[Cu (thr)] ₂ ²⁺	233
2	[Cu (tyr)] ₂ ²⁺	235
3	[Cu (trp)] ₂ ²⁺	247
4	[Cu (his)] ₂ ²⁺	256

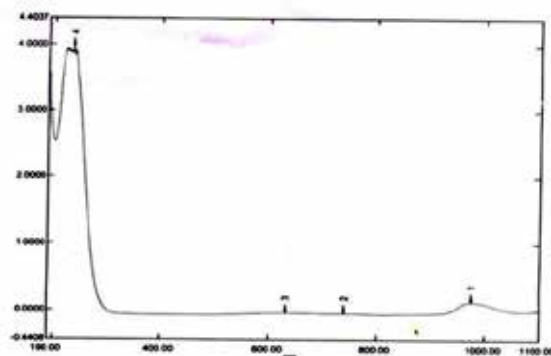


Fig. -1: Uv-vis Spectra of [Cu (thr)₂]²⁺

Table (3): IR-frequencies (in cm⁻¹) of Copper complexes

SN	Complex	Group	Band cm ⁻¹
1	[Cu (thr)] ₂ ²⁺	N-H (bending) bounded with metal	1585
		N-H (stretching)	3245-3381
		C=O bounded with metal	1627
2	[Cu (tyr)] ₂ ²⁺	N-H (bending) bounded with metal	1584
		N-H (stretching)	3264-3383
		C=O bounded with metal	1623
3	[Cu (trp)] ₂ ²⁺	N-H (bending) bounded with metal	1581
		N-H (stretching)	3269-3382
		C=O bounded with metal	1626
4	[Cu (his)] ₂ ²⁺	N-H (bending) bounded with metal	1586
		N-H (stretching)	3276-3379
		C=O bounded with metal	1686

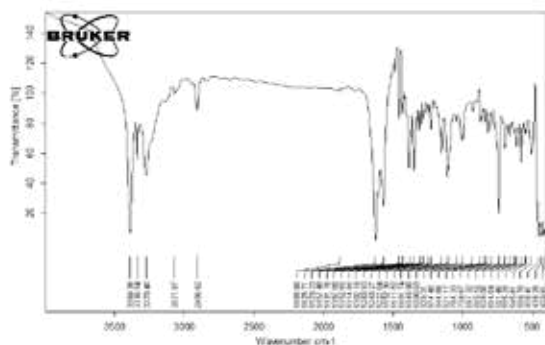
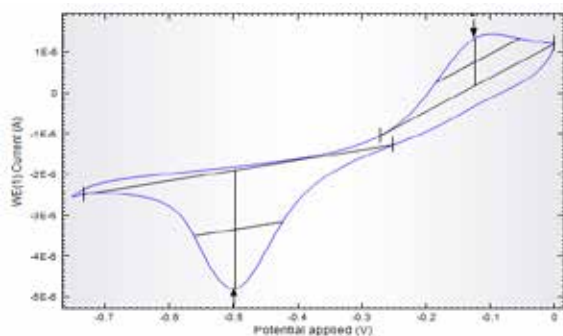
Fig.-2 IR Spectra of $[Cu(trp)_2]^{2+}$

Table (4): CV results (in mV) for Cu(II) complex.

SN	Complex	Reduction Peak(B1)	Oxidation Peak(A1)	Peak (1/2)	Peak width (1/2) V
1	$[Cu(thr)_2]^{2+}$	0.12463	-0.49803	0.061202	0.13778
2	$[Cu(tyr)_2]^{2+}$	-0.12934	-0.49564	-0.07422	0.14363
3	$[Cu(trp)_2]^{2+}$	-0.13186	-0.50298	0.065614	0.13789
4	$[Cu(his)_2]^{2+}$	-0.13187	-0.46636	0.082231	0.16978

Fig - 3 : Cyclic voltammogram of $[Cu(tyr)_2]$ **Conclusion:**

In recent years the importance of metal ions and their complexes have the approaches to increases the efficacy of the drugs consists in their modification of physical and chemical factors. Latest researches in this area focus on the synthesis and characterization of biological compounds containing metal ions, due to their applicability in pharmacy. In this paper there is an increased focus on studies carried out on the complexation of Cu(II) with amino acids (L-threonine, L-tyrosine, L-tryptophane, L-histidine). The coordination of the copper (II) with amino acids arises from the shift of the $\nu_s(C=O)$, $\nu_s(C-N)$ 1623 and 1586 cm^{-1} respectively. The cyclic voltammogram represents only reduction peak at -498.03mV. The broad band is observed at 16,638 cm^{-1} in the electronic spectrum of the Cu(II) complex assigned to ${}^2E_g - {}^2T_{2g}$ transition which is conform the octahedral geometry of all the complexes (Dunn et al 1960).

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