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Synthesis, Characterization of Some Complexes of Copper (II) with L-Asparginine, L-Histidine, L-Lysine

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ABSTRACT

Cu(II) complexes are interesting due to their biologically active and deliberated interest in the research due to their coordination properties. Because these complexes have high pharmacological potential and act as good chelating agents. A series of complexes of Cu(II) with essential amino acids, where L (L-Asparginine, L-Histidine, L-Lysine) and M (Cu^{2+}), have been prepared with formula $[M(L)_2]^{2+}$. The complexes were synthesized and characterized by elemental chemical analysis, electronic and infrared spectra.IR spectroscopy confirms the ligand coordination to the metal ions through carboxyl and amine groups.

Keywords: Copper (II), Amino acids, IR, UV and CV.

INTRODUCTION

Latest researches in these areas focus on the synthesis and characterization of biological compounds containing metal ions, due to their applicability in pharmacy, medicine, agronomy and nutrition. The modern chemotherapy is promoted on the basis of metals and metal complexes which play a key role in the pharmacological properties of known drugs. There are many metal ions are play very important roles in biological activities in the human body[1,2]. Cu (II) complexes have attract attention due to their biological applications and coordination modes. When it bound to metals and act as high pharmacological and good chelating agents. Complexes of Cu (II) with amino acids are used as models to study the pharmacological effects of drugs and lowering toxic effects of some metal ions [3,4]. Amino acid coordinates to metals it confirms structural lability[5] and also have applicability in enzyme inhibition[6,7]. These complexes have a vast area in pharmacological and toxicological properties that has drawn lot of current attention[8-12]. 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-Asparginine, L-Lysine and L-histidine as ligands. This paper has increased focus on the complexation of Cu (II) with amino acids and characterization by elemental analysis, CV, IR, UV-Visible.

EXPERIMENTAL

Materials and Methods

Chemicals

Cu $(NO_3)_2.3H_2O$, $CuSO_4.5H_2O$, $CuCl_2$, sodium acetate, L- Asparginine, L-Histidine, L-Lysine were purchased from alfa acear, Great Britain. All solvent were HPLC grade and used further purification.

Synthesis of complexes

It is generally known that a metal ion can bind two amino acids to form a complex (Fig. 1). Therefore, amino acid-metal complexes were prepared in the deionized water by reacting the corresponding amino acid and metal ion in a 1:2 molar ratio. The $[Cu\ (L)_2]^{+2}$ complexes were prepared from four different salts of copper and amino acids (L- Asparginine, L-Histidine, L-Lysine) as ligand. In this process 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 2 ml aqueous solution of 1 mM of metal salt was added drop by drop into that solution with continuous string for 3 hours. A dark 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 recorded by the KBr method using a Bruker Alfa-T model Fourier transform (FT-IR) spectrometer (Bruker Instrument Germany). The spectrometer was equipped with a Glober IR source, KBr beam spillter 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-visible spectroscopy

The UV-Visible transmittance spectra of the complexes were recorded 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 voltammetry

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

RESULTS AND DISCUSSION

Characterization of metal complexes

All the complexes are single colored, non-hygroscopic and thermally stable solids. The analytical data of these complexes were given in table-1 which indicating metal-ligand bonding. The complexes are insoluble in common organic solvents but fairly soluble in H_2O and DMSO.

UV-visible spectroscopy

The symmetry around the metallic ions was determined comparing the amino acid and metallic complexes UV-Visible

spectra. The electronic spectra of the complexes were recorded in DMSO and their assignments were given in table-2. One representative ligand field spectra of $[Cu(his)_2]^{2+}$ is shown in Fig.-2 and band position are presented in table-2. Characteristic $\pi-\pi^*$ transitions are observed in the spectrum of complexes at 257, 288, and 364 nm[13,14]. The electronic spectrum also exhibits a broad band at 815 nm attributable to d-d transitions, which strongly distorted the octahedral geometry around the Cu (II) ion[15]. The UV-Visible spectra of the complexes show absorption bands assigned to a large band around 634 nm (16000 cm-^{1}). The presence of the later band mentions an octahedral stereochemistry for these complexes[16]. The absorption bands of the complexes corresponded to the n→σ*, n→π* and π*→π* transitions of -NH_2 and -COO, Shifts in these bands and the observed *d-d* transitions of the complexes, presented in table-2, indicated coordination.

Infra red spectroscopy

The IR spectrum of amino acids exhibits significant features in υNH3 and υC=O regions. The amino acids exist as zwitterions in solution and in solid state. The IR spectra of amino acids exhibited significant features in υNH3 and υCOO– regions[17]. In histidine (table 2) the peaks at 3130 cm^{-1}, 3009 cm^{-1} were ascribed to N-H symmetric and asymmetric stretching vibrations and 1588 cm^{-1} and 1413cm^{-1} for carboxylate group of histidine. The peak due to imidazole in plane was observed at ~964 cm^{-1}. NH_3^+ twisting and rocking and COO– wagging frequencies were observed in the range 1200–600 cm^{-1}. In coordination chemistry Infrared studies of the complexes of amino acids have shown that a useful tool in structural studies[18]. The spectra exhibited a marked difference between bands belonging to the stretching vibration of υ (N-H) of the amine group in the range between 3448-3383 cm^{-1}, suggesting the possibility of the coordination of ligand through the nitrogen atom at the amine group[18-20]. 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[21-23]. The infrared spectra of the complexes (1), (2) and (3) is given in Fig.-3, 4 and 5 respectively. The absorption band at 1624 cm^{-1} was ascribed to the υ(C=O) stretching vibration in the spectrum. 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 assignment of the complex 1, 2 and 3 are mentioned in table-3.

Electrochemical studies of complexes

Fig-6, 7 and 8 show 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 and $[Cu(II)L_2]^{2+}$ system at different pH i.e. isoelectric point of amino acids. In this scan range, the CVs show a single reduction peak (B1) at -498.05 for complex 1, 495.61 for complex 2 and 466.31 mV for complex 3. The forward sweep only one oxidation waves A1 found at 124.51 for complex 1, 129.39 for complex 2 and 131.84 mV/s for complex 3 at the scan rate of 0.01 V/s. Voltamogram clearly represents that reduced moiety of Cu (II) does not fully oxidized in further sweep.

CONCLUSIONS

Complexes of metal ions with amino acids can be assigned as a perfect models to study the pharmacological active effects of drugs and also lowering toxic effects. The considerable fact is interactions between transitional metal ions and amino acids are

very interesting in the biological applications. A series of complexes of Cu(II) and amino acid i.e. L-Aspargine, L-Histidine and L-Lysine with formula $[Cu(L)2]^{+2}$ have been synthesized and characterized on the basis of elemental chemical analysis, infrared spectra, UV-Visisble and cyclic voltametery 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.

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

S. No.	Complex	Empirical formula	Molecular weight	Color	Elemental analysis Calculated (Found)			
					M %	C %	H %	N%
1.	$[Cu(asp)_2]\ 2SO_4$	$C_8H_{30}N_4O_{11}Cu$	549.97	Shining blue	11.55	15.36 (14.45)	5.45 (6.77)	10.18 (9.67)
2.	$[Cu(asp)_2]\ 2Cl$	$C_8H_{20}N_4O_7Cu$	434.73	Royal blue	14.61	22.08	4.6	12.88
3.	$[Cu(asp)_2]\ 2NO_3$	$C_8H_{26}N_4O_7Cu$	541.88	Shining blue	11.72	17.71	4.79	10.33
4.	$[Cu(asp)_2]$ $2CH_3COO$	$C_8H_{22}N_4O_7Cu$	499.93	Deep blue	12.70	19.20	4.40	11.23
5.	$[Cu(his)_2]\ 2SO_4$	$C_{12}H_{28}N_6O_9Cu$	559.99	Shining brown	11.34	17.14	5.21	15.00
6.	$[Cu(his)_2]\ 2Cl$	$C_{12}H_{28}N_6O_4Cu$	444.75	Shining brown	14.28	32.37 (15.67)	6.29 (29.6)	18.88 (12.43)
7.	$[Cu(his)_2]\ 2NO_3$	$C_{12}H_{24}N_6O_9Cu$	474.51	Light brown	13.59	30.34	5.05	17.70
8.	$[Cu(his)_2]\ 2CH_3COO$	$C_{12}H_{20}N_6O_5Cu$	509.95	Shining brown	12.46	28.23	3.92	16.37
9.	$[Cu(lys)_2]\ 2SO_4$	$C_{12}H_{42}N_4O_{11}Cu$	578.11	Crystalline blue	10.95	24.90	7.26	9.68
10.	$[Cu(lys)_2]\ 2Cl$	$C_{12}H_{32}N_4O_6Cu$	462.87	Crystalline blue	13.72	31.11	6.91	12.09
11.	$[Cu(lys)_2]\ 2NO_3$	$C_{12}H_{38}N_4O_7Cu$	570.02	Crystalline blue	11.14	25.26 (29.92)	6.68 (6.79)	9.82 (8.27)
12.	$[Cu(lys)_2]\ 2CH_3COO$	$C_{12}H_{34}N_4O_5Cu$	528.07	Light blue	12.03	27.26	6.43	10.60

Table 2. λmax (nm) values for Cu (II) complexes

S. No.	Complex	λmax(nm)
1	$[Cu\ (asp)_2]^{2+}$	257
2	$[Cu\ (his)_2]^{2+}$	288
3	$[Cu\ (lys)_2]^{2+}$	364

Table 3. IR-frequencies (in) of Cu (II) complexes

S. No.	Complex	Stretching and bending	Frequency in cm^{-1}
1	$[Cu\ (asp)_2]^{2+}$	N-H (bending) bounded with metal	1586
		N-H (stretching)	3267-3368
		C=O bounded with metal	1632
2	$[Cu\ (his)_2]^{2+}$	N-H (bending) bounded with metal	1584
		N-H (stretching)	3243-3376
		C=O bounded with metal	1637
3	$[Cu\ (lys)_2]^{2+}$	N-H (bending) bounded with metal	1582
		N-H (stretching)	3267-3385
		C=O bounded with metal	1631

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

S. No.	Complex	Reduction Peak(B1)	Oxidation Peak(A1)	Peak (1/2)	Peak width (1/2) V
1	$[Cu (asp)_2]^{2+}$	0.12451	-0.49805	0.061204	0.13685
2	$[Cu (his)_2]^{2+}$	0. 12939	0.495.61	-0.07324	0.14353
3	$[Cu (lys)_2]^{2+}$	0.131.84	-0.46631	0.065627	0.13812

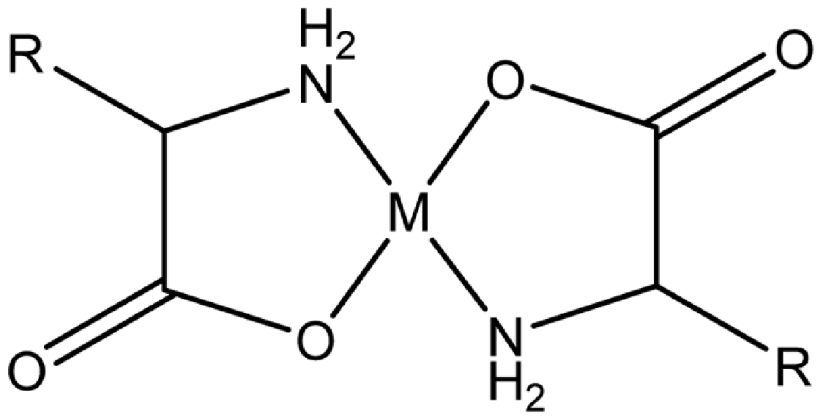

Figure 1. General structure of the amino acid-metal complex

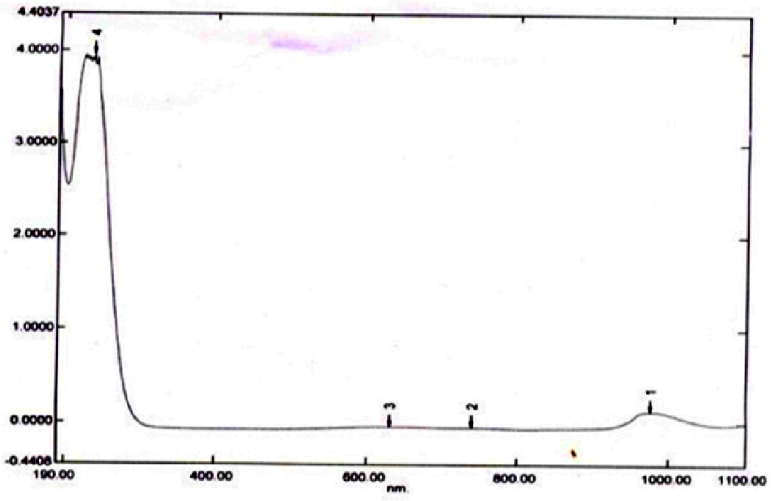

Figure 2. UV-Visible Spectra of $[Cu (his)_2]^{2+}$

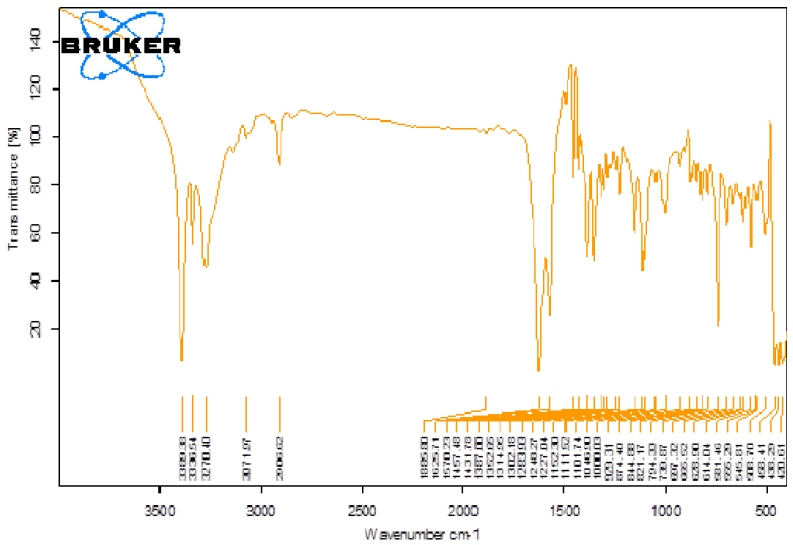

Figure 3. IR Spectra of $[Cu\ (asp)_2]^{2+}$

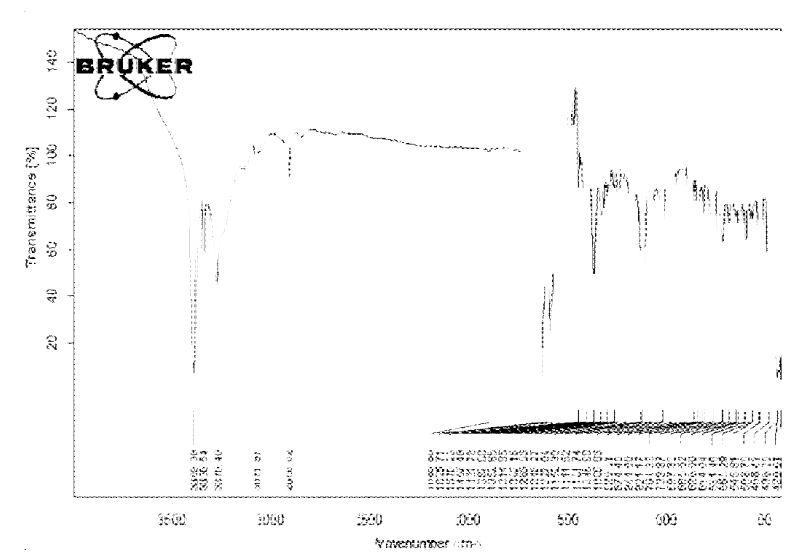

Figure 4. IR Spectra of $[Cu\ (his)_2]^{2+}$

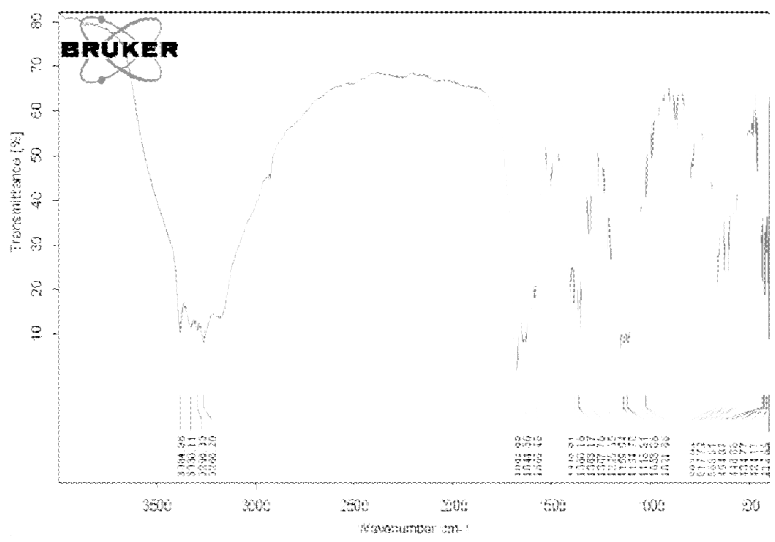

Figure 5. IR Spectra of $[Cu\ (lys)_2]^{2+}$

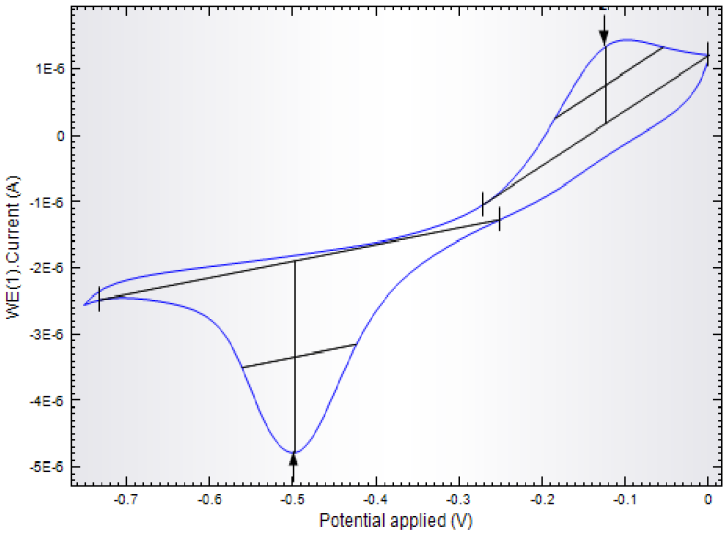

Figure 6. Cyclic volatammogram of $[Cu\ (asp)_2]^{2+}$

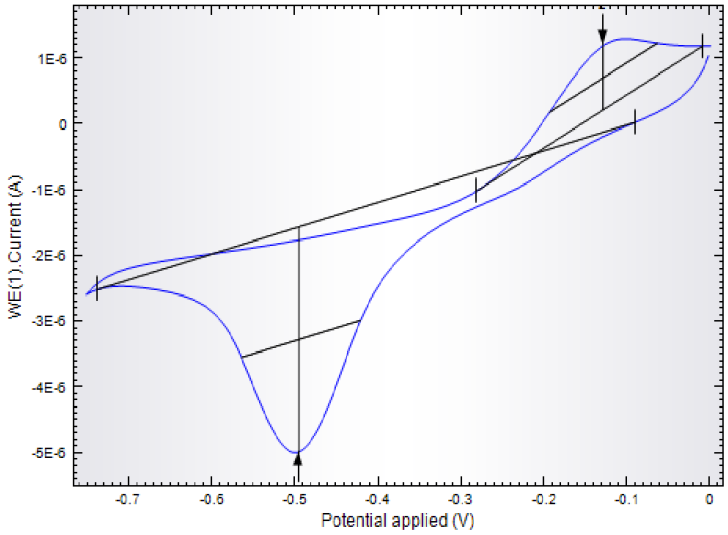

Figure 7. Cyclic volatammogram of $[Cu\ (his)_2]^{2+}$

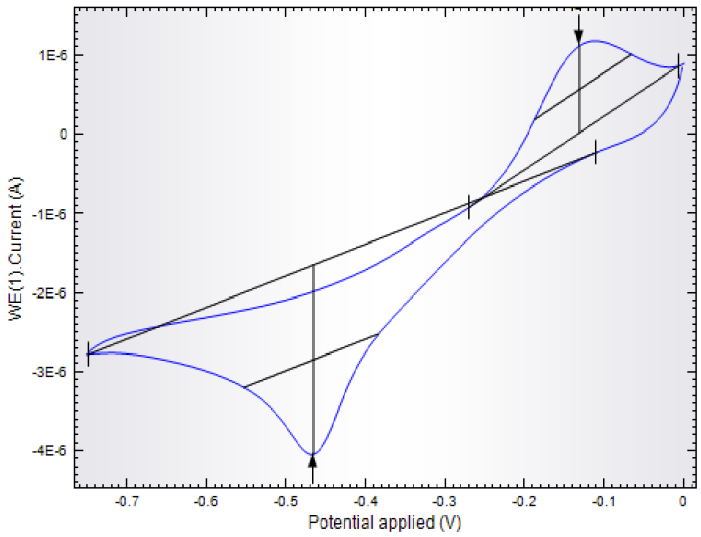

Figure 8. Cyclic volatammogram of $[Cu\ (lys)_2]^{2+}$