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Synthesis and Characterization of Some Zn(II) Complexes of L-Glutamic Acid and L-Aspartic Acid

I P Tripathi[1], Aparna Dwivedi[2] and Mahendra Kumar Mishra[2]

[1]Dean, Faculty of Science & Environment, MGCGV Chitrakoot, Satna [MP], India

[2]Researchers, Faculty of Science & Environment, MGCGV Chitrakoot, Satna [MP], India

Abstract

Medicinal inorganic chemistry is a discipline in which metal complexes are used in therapeutic and diagnostic medicine. In development of modern chemotherapy metal and their complexes have played key role. The metal based drugs are also being used or the treatment of variety of ailment viz. diabetes, rheumatoid arthritis, inflammatory and cardiovascular diseases as well as diagnostic agents.

Keywords: Elemental analysis, Cyclovoltammetry, UV and IR spectroscopy.

1. Introduction

Inorganic compounds play significant role in biological processes, and it has been recognized from several studies that many organic compounds used in medicine are activated or biotransformed by metal ions metabolism [1]. Zinc is one of the essential trace elements and exists in metalloproteins and active sites of different metallozymes [2]. Amino acids are basic unit of protein. Amino acids contain an amino group and a carboxylic group. Amino acids play key role in regulating several processes associated to gene expression and modulation of the function of the proteins that mediate messenger RNA (mRNA) translation [3]**.** When trace elements like copper, iron, zinc and other are chemically bonded to amino acids with two bonds from each amino acid, forms chelate. All of naturally occurring α- amino acids binded in a specific way is recognized as the glycinato way. This means that a five- membered ring is formed with the metal, amine nitrogen and the carboxylic oxygen. [4, 5]

Current research is based on synthesis and characterization of some Zn(II) complexes of l-amino acids.

2.Material & Methodology

Required chemical

L- glutamic acid, L- aspartic, zinc sulphate, zinc chloride, zinc acetate were purchased from SRL, India.. All chemicals viz., ethanol, sodium acetate, sodium hydroxide, water were synthetic grade and used without further purification.

Synthesis of complexes

Complexes were prepared by stirring method Metal complexes synthesized from different salts (chloride, sulphate and acetate) of Zn(II) and l-amino acids. 2 mM solution of ligand was taken in a beaker and stirred till clear solution after that 1 mM aqueous solution of metal salt was added drop by drop with continuous stirring and stirred for three hours. White/cream/pale yellow color solution was obtained which was transferred in a petri dish, to remove solvent put in incubator at 45 ^{o}C. Dried complexes obtained in the form of crystalline solid which was collected in vials and stored in desiccator. [6, 7, 8]

Characterization of synthesized metal complexes

Elemental analysis

Elemental analysis were carried out on an element analyzer Euro Vector EA 3000 at CDRI Lucknow [UP] to know the percent of carbon, hydrogen and Nitrogen in synthesized complexes.[8]

Infrared Spectroscopy

Infrared (IR) spectra were carried by the KBr method via a Bruker Alfa-T model Fourier transform (FTIR) spectrophotometer (Bruker Instrument, Germany). The spectrometer was outfitted with a Global IR source, KBr beam splitter, and detector. For each spectrum, 16 scans were taken with the resolution of 4 cm-^{1}. The obtained IR

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spectra were processed by means of the program OPUS 7.0 at research lab MGCGV Chitrakoot Satna [M.P.]. [8,9]

UV-Visible Spectroscopy

The UV-visible transmittance spectra of the complexes were recorded at 25 ^{0}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 at research lab MGCGV Chitrakoot Satna [M.P.]. [8, 9]

Cyclovoltammetry

The cyclicvoltametric measurements were carried out with a Metrohm Instrument (Germany) having an electrochemical cell with a three-electrode system. The reference electrode was an Ag/AgCl2. Platinum wire used an 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 voltamograme, peak position and area were calculated using NOVA 1.9 software at research lab MGCGV Chitrakoot Satna [M.P.]. [8]

3. Result & Discussion

The Complexes were prepared with l-amino acids using three salt of zinc i.e ($ZnSO_4.7H_2O$ (A), $Zn(CH_3COO)_2.2H_2O$ (B) and $ZnCl_2$ (C)) in aqueous solution. It is assumed that synthesized complex of an amino acid was same for all three salt so complexes were differentiate to identify by (A), (B) and (C) for $ZnSO_4.7H_2O$, $Zn(CH_3COO)_2.2H_2O$ and $ZnCl_2$ respectively. Characterization of synthesized metal complexes and their biochemical activity has been evaluated and described separately.

Characterization of synthesized metal complexes

All synthesized complexes were in white/cream/pale yellow colored, non-hygroscopic and thermally stable solids. The complexes were semi soluble in common organic solvents such as methyl/ethyl alcohol but were fairly soluble in H_2O, DMSO and DMF. Complexes were analyzed by means of elemental analysis, IR, UV-VIS spectroscopy and Cyclovoltammetry.

Elemental analysis

Elemental analysis was done by Element analyzer Euro Vector EA 3000 (Italy) at CDRI Lucknow [UP]. The elemental analysis measurements confirm the percentage presence of carbon, hydrogen and nitrogen in our synthesized complexes. We have calculated percentage of C, H, N, O, S and Zn by formula and compare with the found elemental data of C, H and N. Calculated data of C, H and N have shown some differences with respect to found data of C, H and N, it may be due to presence of some impurities in metal complexes. Elemental data of the synthesized Zn(II) complexes of amino acids are given in Table- 1.

Table-1: Elemental analysis data of Zn(II) complexes with L – Amino acids

SN	Complex	Formula in Hill system	Molar Mass (g/mol)	Color	Mass Percent of Elements Calculated (Found)					
					H%	C%	N%	O%	S%	Zn%
1	$[Zn(Asp)_2]$(A)	$C_8H_{14}N_2O_8Zn$	331.59	White	4.26 (4.86)	28.98(27.23)	8.45(8.53)	38.06	-	19.72
2	$[Zn(Asp)_2]$(B)	$C_8H_{14}N_2O_8Zn$	331.59	White	4.26 (4.22)	28.98(27.23)	8.45(7.94)	38.06	-	19.72
3	$[Zn(Asp)_2]$(C)	$C_8H_{14}N_2O_8Zn$	331.59	White	4.26 (3.69)	28.98(27.00)	8.45(9.12)	38.06	-	19.72
4	$[Zn(Glu)_2]$(A)	$C_{10}H_{18}N_2O_8Zn$	359.65	White	5.04 (6.88)	33.40(32.18)	7.79(8.88)	35.59	-	18.18
5	$[Zn(Glu)_2]$(B)	$C_{10}H_{18}N_2O_8Zn$	359.65	White	5.04 (6.24)	33.40(33.92)	7.79(6.00)	35.59	-	18.18
6	$[Zn(Glu)_2]$(C)	$C_{10}H_{18}N_2O_8Zn$	359.65	White	5.04(5.64)	33.40(32.96)	7.79(7.22)	35.59	-	18.18

UV-Visible Spectroscopy/ Electronic Spectra

1. The UV-Vis absorption spectra of L-amino acids and its Zn(II) complexes in 100% DMSO were recorded at room temperature . In the electronic spectroscopy, the geometry of the metal complexes can be found out using the d-d transitions. However, the Zn(II) complexes due to the completely filled d^{10} configuration, do not exhibit d-d transition and show no absorption band above 400 nm. As d-d transition is not expected in Zn (II) complexes hence complex is expectedly diamagnetic and exhibit charge transfer spectra, L → M charge transfer transition correspond to tetrahedral structure [10, 11, 12, 13, 14, 15, 16]

The λ_{max} value Zn(II) complexes of amino acids are shown in table 2 and electronic spectra are shown in Fig. 1and 2.

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Table 2: λ_{max} (nm) values for Zinc(II) complexes of Amino Acids

SN	Compounds	λ_{max} (nm)
1	$[Zn(Asp)_2](A)$	206
2	$[Zn(Asp)_2](B)$	206
3	$[Zn(Asp)_2](C)$	204
4	$[Zn(Glu)_2](A)$	206
5	$[Zn(Glu)_2](B)$	206
6	$[Zn(Glu)_2](C)$	198

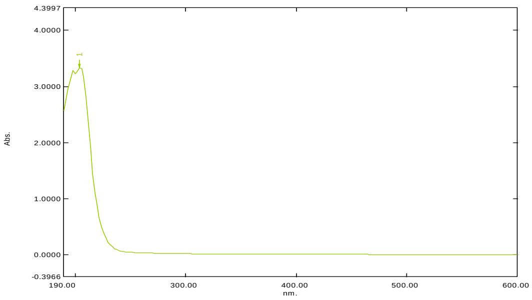

Fig-1: Ultraviolet spectra of $[Zn(Asp)_2](B)$

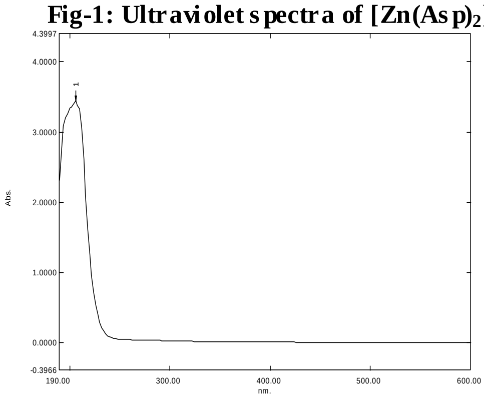

Fig-2: Ultraviolet spectra of $[Zn(Glu)_2](C)$

Infrared spectroscopy is important tool to characterize metal complexes. All the assignments of characteristic peaks have been done on the basis of published research articles. We have found significant shifting of carbonyl group (C=O) and NH_3^+ group from their original position with respect to free l-amino acids which confers the coordination of these groups to metal and formation of new complex. The IR spectra of the Zn(II)complexes of amino acids were compared with the IR spectra of l-amino acids to determine the changes that might have taken place during the complexation. On complexation, the asymmetric and symmetric stretching bands of carboxylato groups were shifted to lower frequency in some complexes, which reveals the formation of a linkage between the metal ion and carboxylato oxygen atoms. [16]. The band around 1650-1515 cm^{-1} is characteristic of the azomethine nitrogen atom present in the free ligand[17]. However the spectra of some complexes exhibited a marked difference between 3469- 3334 cm-1 bonds belonging to the stretching vibration of (N-H) of the amine group in the range. The N-H stretching vibration in the complexes was shifted to higher frequencies with the complexes, suggesting that the coordination of the metal ion with the ligand was via the nitrogen atom [18, 19, 20, 21, 22]. The broad band appeared around 3200-3600 cm^{-1} in the metal complexes can be recognized to the stretching vibration of the coordinated water molecules. Also bands below 1000 cm^{-1} in the complexes are assigned to C-C stretching [23, 24, 25].

The infrared spectra of the l-amino acids and the Zn complexes of amino acids are given in fig 3-6, important absorption bands of Zn(II) complexes of amino acids are listed in Table - Table 3 and 4.

Infrared Spectroscopy

Table-3: IR Frequencies (in cm^{-1}) of Zn(II) complexes with L-Aspartic acid

S.N.	IR frequency (cm^{-1})					Group Assignment
	L- Aspartic acid		$[Zn(Asp)_2]$ (A)	$[Zn(Asp)_2]$ (B)	$[Zn(Asp)_2]$ (C)	
	Reported (26)	Found				
1	3124	-	3120	-	-	$vs(NH_3^+)$
2	3054	-	-	-	-	$vs(NH_3^+)$
3	3018	3013	-	-	-	$\upsilon(OH)$
4	2956	-	2926	-	2925	$us(CH_2)$
5	1691	1678	-	-	-	$\upsilon(CO)$
6	1643	-	1627	1594	1622	$\delta(NH_3^+)$
7	1510	-	-	-	-	$\delta(NH_3^+)$
8	1459	-	-	-	-	$\delta(CH_2)$
9	1421	-	1412	1415	1424	$\upsilon(CO_2^-)$
10	1407	-	-	-	-	$\upsilon(CO)+\delta(OH)$
11	1357	-	1352	-	1353	$\delta(CH)$
12	1333	-	-	-	-	$\delta(CH)$
13	1247	-	1228	1226	1229	$t(CH_2)$
14	1150	-	1131	-	1143	$\rho(NH_3^+)$
15	1077	-	-	1089	1099	$\upsilon(CN)$
16	898	898	902	904	902	$\upsilon(CC)$
17	870	873	853	864	853	$\rho(CH_2)$

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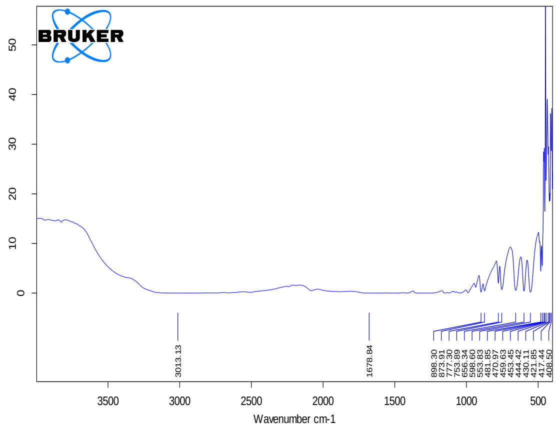

Fig-3: Infrared spectra of L-Aspartic Acid

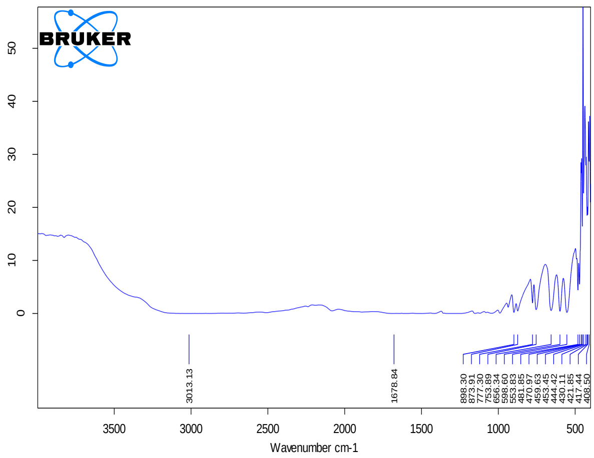

Fig-4: Infrared spectra of $[Zn(Asp)_2](C)$

Table-4: IR Frequencies (in cm^{-1}) of Zn(II) complexes with L - Glutamic acid

S.N.	IR frequency (cm^{-1})					Group Assignment
	L- Glutamic acid		$[Zn(Glu)_2]$ (A)	$[Zn(Glu)_2]$ (B)	$[Zn(Glu)_2]$ (C)	
	Reported (27)	Found				
1	2962	2910	2926	-	2925	υ (CH)
2	1663	1685			-	$\delta(NH_3^+)$
3	1641	1634	1622	1594	1627	v(CO)
4	1437	1456	-	-	-	$\delta(CH_2)$, sciss.
5	1420	1424	1424	1412	1415	$vs(CO_2^-)$
6	1375	1373	1352	1353	1353	$\delta(CH_2)$
7	1313	1308	1304	1310	1311	δ(OH)
8	1261	1274	1228	1229	1226	δ(CH)
9	1151	1163	1131	-	1143	$\delta(NH_3^+)$, rock
10	1078	1076	-	1090	-	v(C0)
11	913	911	-	-	-	v(CC)
12	868	859	853	864	853	$\delta(CO_2^-)$
13	808	818	816	834	817	v(CC)
14	713	714	-	-	-	CH_2 rock
15	673	671	668	-	669	$\delta(CO_2^-)$
16	540	534	-	-	-	γ(occ)
17	513	511	-	-	-	δ(COOH)

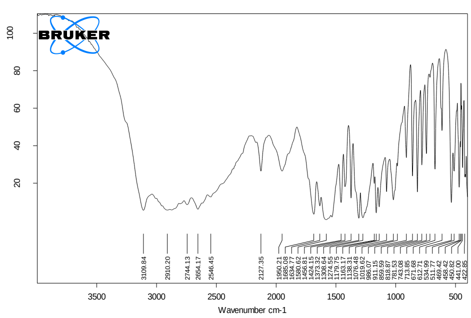

Fig-5: Infrared spectra of L-Glutamic Acid

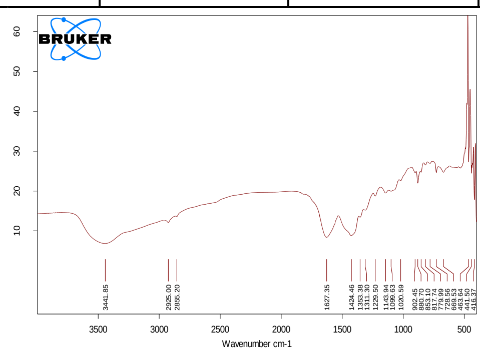

Fig-6: Infrared spectra of $[Zn(Glu)_2](C)$

Cyclovoltammetry

Cyclic voltammetry is a useful technique to study redox behavior of metals and their complexes

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with various ligands [28]. The electrochemical processes are not only controlled by adsorption and diffusion but also obviously affected by dissolved oxygen, pH, and temperature [29]. The electrochemical behavior of all complexes has been studied by cyclic voltammetric techniques using a platinum wire electrode in electrolyte in water under an inert atmosphere. Zinc can form poly-metal complexes through the interactions with interior amino groups and the maximum coordination number of metal ions [30]. The important parameters of a cyclic voltammogram are the magnitudes of the anodic peak current (ipa), cathodic peak current (ipc), anodic peak potential (Epa) and cathodic peak potential (Epc). All the complexes show simple irreversible wave for Zn^{2+} redox potential in 0.00 to 2.00 V potential range and scan rate were 0.100 V/S. In the electrochemical potential cathodic potential denoted as Epc and anodic potential denoted as Epa. Change in electronic potential (ΔEp) calculated by the substraction of anodic and cathodic peaks, $Ep_{1/2}$, taken as the average of Epc and Epa. All CV data are given in Table – 5 and voltammogram of all Zn(II) complexes are shown in Fig 7 and 8.

Table - 5: CV data (in V) for Zn(II) complexes of L-Amino Acids

SN	Complex	Epc (V)	Epa (V)	ΔEp (V)	$Ep_{1/2}$ (V)
1	$[Zn(Asp)_2](A)$	1.3448	1.0152	0.3296	1.1800
2	$[Zn(Asp)_2](B)$	1.3621	1.0234	0.3387	1.1927
3	$[Zn(Asp)_2](C)$	1.3789	1.0054	0.3735	1.1921
4	$[Zn(Glu)_2](A)$	1.2958	0.9613	0.3345	1.1285
5	$[Zn(Glu)_2](B)$	1.2909	0.9564	0.3345	1.1236
6	$[Zn(Glu)_2](C)$	1.3153	1.0663	0.2490	1.1908

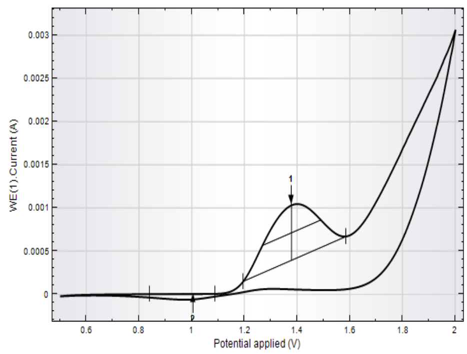

Fig-7: Cyclovoltagramm of $[Zn(Asp)_2](C)$

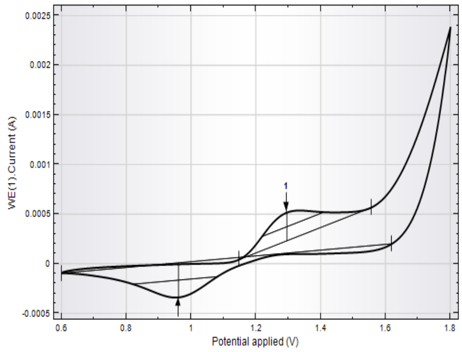

Fig-8: Cyclovoltagramm of $[Zn(Glu)_2](A)$

4. Conclusion

Chelation reduces the polarity of the metal ion by partial sharing of its positive charge with the donor group of ligands, therefore it is concluded on the bases of the chelate theory, that increasing the number of chelate rings may improve the biochemical activities of metal complexes. Metal-based compounds may also be used as potent antibacterial, antifungal, and anticancer drugs, or as imaging agents.

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