



Synthesis, Characterization and Stability Constants of Nickel (II) Complexes of Common α -Amino acids

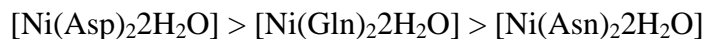
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ABSTRACT

The Ni(II)-complexes of α -amino acids: L-Asparagine (L-*HAsn*), L-Glutamine (L-*HGln*) and Aspartic acid (L-*H₂Asp*) were synthesized by easy, efficient, clean and environmentally benign method. The synthesized complexes were characterized by elemental analysis, conductivity measurements, magnetic moment and spectral analysis. The elemental analysis data of the investigated complexes revealed their 1:2 (metal to ligand) stoichiometries and monomeric nature and very low molar conductance values show the non-electrolytic nature of the complexes. The infrared spectral studies revealed the monobasic bidentate (N & O donor) nature of the amino acid ligands which coordinated through amino-N and carboxylate-O with Ni²⁺ ion in the complexes. The magnetic moment values and electronic spectral studied indicated the octahedral geometry of the investigated complexes. These complexes contain 5-membered chelate rings formed via the coordination of amino-N and carboxylate-O donors. The overall stability constants, which are the products of the stepwise stability constants of the octahedral ($K_1 \times K_2$) metal-amino complexes, are very high, revealing good stability and the stability order of the complexes is as follows:



KEY WORDS: Amino acids, Transition metal complexes, Octahedral complexes, Stability constants

INTRODUCTION

Nearly all the proteins are the polymer of twenty common amino acids (L-amino acids). Thus, the amino acids are the structural and functional chemical entities (monomers or units) of proteins which are the basis of living organisms. Evidently, the α -amino acids are the essential for almost all biochemical processes in living organisms [1]. Further, the α -amino acids are very nice chelating agents due to the presence of amino and or carboxylate groups in their molecules. That is why they coordinate to the transition metal ions through amino and or carboxylate groups and form complexes. The literature survey revealed that the complexation of amino acids with transition metal ions have been extensively studied in a few decades [2-4]. The enzymatic activity and stability of protein structure are related with the amino acid-metallic ion interactions and the metal-amino acid complexes are the basis model systems in biological systems [5-9].

The stability of amino acid-metal complexes leads the quality of existing vitamins and thus serving as the chemotherapeutic agents in the drug design, nutrition, medical and pharmacological fields [10-11]. That is why the coordination chemists have been attracted towards the study amino acid-metal complexes. Amidst the abundant literature on the transition metal complexes of amino acids, very few reports have been found till date on the complexation reactions and stability constants of α -amino acid-transition metals in environmental benign media and methods.

As a part of our continuing efforts to synthesize and characterize transition metal complexes using amino acids as ligands [12-13], the present research article describes the structure elucidation and stability constants of nickel (II) complexes of α -amino acids: L-Asparagine (L-*HAsn*), L-Glutamine (L-*HGln*) and Aspartic acid (L-*H₂Asp*) (Table-1) synthesized through environmentally benign methods. Although, single crystal of the investigated complexes could not be isolated from any solutions; however, analytical data, magnetic data and spectroscopic studies enable us to propose possible geometries of the investigated complexes.

Table-1

Amino acids used as ligands

Name of amino acids	L-Asparagine	L-Glutamine	L-Aspartic Acid
Symbol	N	Q	D
Abbreviation	<i>HAsn</i>	<i>HGln</i>	<i>H₂Asp</i>
Isoelectric Point	5.4	5.7	2.8

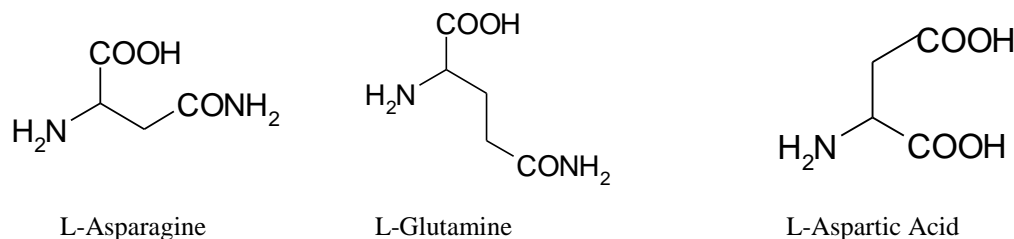


Figure-1: Structure of the ligands

EXPERIMENTAL

Materials & Method

All the used chemicals and solvents were of Anal R grade. The amino acids *L-Asparagine* (*HAsn* or *N*), *L-Glutamine* (*HGln* or *Q*) and *L-aspartic acid* or *aspartate* (*H₂Asp* or *D*) were purchased from Loba Chemie which were used as received without further purification. The metal salt and amino acid solutions were prepared by direct dissolution in doubly distilled water. Metal salt was obtained from S.D. Fine chemical, Mumbai. Solvents were purified and dried according to standard procedure [14].

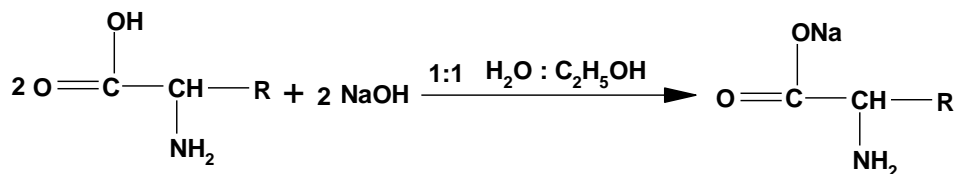
All the investigated compounds were analyzed satisfactorily for C, H, X and N using Carl-Ebra 1106 elemental analyzer in micro analytical laboratory. Metal and chloride contents of the transition metal complexes were analyzed following standard methods [15]. The melting/decomposition points were determined by placing a finely powdered sample in a glass capillary and heating by using a Mel-Temp melting point apparatus and were uncorrected. Molar conductance measurements were taken using 10^{-3} M solution of the complexes in DMSO on Elico-CM 82 Conductivity Bridge at room temperature provided with a dip type conductivity cell fitted with platinum electrodes. Magnetic susceptibility measurements of investigated solid complexes were carried out on a Gouy's balance at room temperature using mercuric tetrathiocyanatocobaltate (II) as the calibrant. Diamagnetic corrections were applied in compliance with Pascal's constant [16].

The solution spectra were measured or recorded at room temperature on Systronic UV-VIS spectrophotometer Type 119 PC based ($\lambda = 200-1000$ nm & band width 2nm) using DMSO as the solvent. The FT-IR spectra were recorded in KBr medium and Nujol mull techniques on a

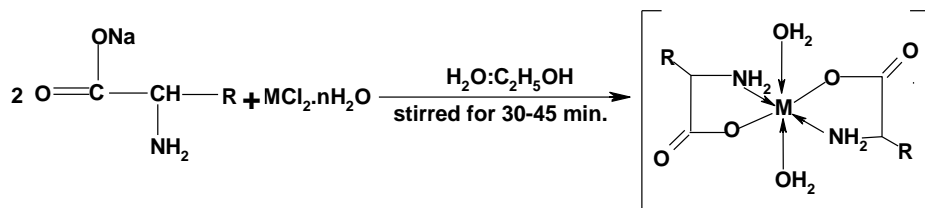
Perkin Elmer RX1 spectrophotometer in wave number region 4000-400 cm^{-1} . The proton nuclear magnetic resonance spectra of complexes were taken in CDCl_3 or D_2O (wherever solubility permitted this) using Hitachi R-600 FT NMR spectrophotometer. Tetramethyl silane (TMS) was employed as the internal reference.

Synthesis of Ni(II) complexes:

A solution of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (1 m mole) in 1:1 mixture of ethanol and water (10 mL) was added to a solution of the ligand (4 mmol) in 20 ml H_2O /ethanol (50%) mixture containing 0.33 mL 30% NaOH (for deprotonation of the amino acids, scheme-1) using stoichiometric amount (1:2) [(metal: 2(Na^+ L)] molar ratio [17]. The reaction mixture was stirred for several minutes (30-45 minutes) at room temperature. After 1.5 hours a coloured crystalline solid was obtained which was filtered and washed with water-ethanol then triethyl ether. The solids were recrystallized from (H_2O :DMSO) (30:70) volumes' mixture and dried in vacuum over anhydrous CaCl_2 (Scheme-2) at 60°C . The yields range from 80 to 90 %. The compounds were found to be soluble in DMSO and hot water (scheme-2).



Scheme-1: Deprotonation of used amino acid ligands



Scheme-2: Synthesis of Ni-complexes of amino acids

Where R = CH_2CONH_2 for N (HAsn), R = $\text{CH}_2\text{CH}_2\text{CONH}_2$ for Q (HGln),
R = CH_2COOH for D (H_2Asp) and M = Ni (II)

Determination of Stability Constants of the Complexes

Into a 400 mL beaker 100 mL of 0.04M, KNO_3 10 mL of 0.02M HNO_3 , 90 mL of distilled water and 1 mmol. (0.001mol.) of nickel (II) chloride hexahydrate were added respectively. 0.05 mL of 0.1M Sodium asparaginate was added and after each addition with

stirring the corresponding pH reading was recorded. The addition of the sodium asparaginate solution was continued until the full 10 mL was added. The sodium asparaginate was prepared by exactly neutralizing a weighed solid asparagine with a calculated amount of standardized 0.1M NaOH and diluting the solution with distilled water to a total volume of 20 mL out of which 10 mL was put into a cleaned and rinsed burette. The same procedure was repeated for each of the remaining amino acids [18].

RESULTS & DISCUSSION

Physical Properties

All the complexes were coloured, non-hygroscopic and thermally stable solids (Table-2). The complexes are insoluble in common organic solvents such as ethyl alcohol, acetone, etc., but are soluble in DMSO and in hot water. The elemental analysis data (Table-2) of metal complexes are consistent with their general formulation as 1:2, monomeric complexes of the type $[\text{Ni}(\text{L})_2 \cdot 2\text{H}_2\text{O}]$. The molar conductance values of the complexes in DMSO at 10^{-3} M concentration are very low indicating their non-electrolytic nature (table-3) [19].

Infrared Spectral Studies

The infrared spectrum of the free ligand exhibited a broad band at $3350\text{--}3400\text{ cm}^{-1}$ which was assigned to the NH_2 stretching frequency. Intense bands at $1490\text{--}1580$ and $1390\text{--}1445\text{ cm}^{-1}$ were observed and are attributed to $\text{COO}^-_{(\text{asy})}$ and $\text{COO}^-_{(\text{sy})}$ stretching frequencies, respectively [20-21].

For the investigated complexes, the COO^- asymmetric stretching frequencies were shifted to lower frequencies compared with that of the ligand. Bands in the region of $345\text{--}315\text{ cm}^{-1}$ indicate the formation of $\text{M}\text{--}\text{O}$ bond and further support the coordination of the ligand to the central metal ion via the oxygen atom of the carboxylate group [22]. Hypsochromic shifts were observed for the --NH_2 frequencies on coordination, for the investigated complexes. This indicates bond elongation on coordination. It therefore suggests probable octahedral geometry for the complexes. New bands in the spectra of the complexes at $460\text{--}560\text{ cm}^{-1}$ were assigned to $(\text{M}\text{--}\text{N})$ stretching frequency. The participation of the lone pairs of electrons on the N of the amino group in the ligand in coordination is supported by these band frequencies [23]. Similarly,

broad sharp bands at 3550- 3640 cm^{-1} in the investigated complexes, obviously shows the presence of coordinated water in the complexes. The new sharp bands appeared at 345-315 cm^{-1} and 460-560 cm^{-1} in the spectra of investigated complexes clearly suggest the formation of (M-O) and (M-N) bonds on complexation (table-4) [24].

¹H- NMR Spectral Studies

In all the ligands, signal of -COOH appeared at 10.95 ppm (δ -scale) but in metal complexes these signals do not appear, probably due to replacement of H^+ by metal ion. The signal due to protons of NH_2 appeared perturbed (decreased) probably due to coordination by N of NH_2 to metal ion [25]. The NMR spectral stud clearly shows the formation of complexes by the ligands. The NMR spectral results are presented in table-5.

Magnetic Moment & Electronic Spectral Studies

The observed values for effective magnetic moment (μ_{eff}) in BM, reported in table-12, suggest the octahedral geometry for Ni(II) complexes [26]. The magnetic moments of the investigated complexes were slightly greater than spin only values due to spin-orbit coupling and it supports the conclusions.

The electronic spectra of the ligands showed three absorption bands at 187-196, 210-216, and 223-232 nm assigned as the $n \rightarrow \sigma^*$, $n \rightarrow \pi^*$, and $\pi \rightarrow \pi^*$ transitions of the major chromophores, NH_2 and COO^- , present in the ligand molecules. On coordination, however, shifts were observed in these bands in addition to $d-d$ transitions bands (Table-13).

The electronic spectra of the investigated complexes in DMSO were recorded in the UV-visible region. The spectra for the investigated Ni(II) complexes displayed three bands at 526-532, 472-476 and 452-456 nm, assigned to ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}$ (F), ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}$ (F) and ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}$ (P) $d-d$ transitions. This was the indicative that the investigated complexes were the mono-nuclear complexes with 6-coordinated octahedral geometry [27]. This proposed geometry was corroborated by their magnetic moment value of 3.06 -3.09 BM. The important electronic spectral bands along with their assignments of the isolated ligands and the complexes under investigation are listed in table-6.

Proposed Geometry of Ni-Complexes

On the basis of the above observations, it is tentatively suggested that investigated Ni(II)- α -amino acid complexes show an octahedral geometry [Figure-2] in which the ligands act as mono-negative bidentate [N & O donor] ligands.

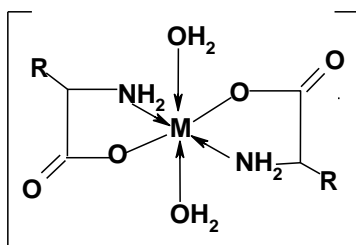


Figure-2: Proposed octahedral geometry (O_h) of the investigated Ni-complexes

Stability Constants of Complexes

All the investigated ligands contain two donor groups (the amino and carboxylate groups), and therefore two hydrogen ions can dissociate from the fully protonated cations of the amino acids (H^2L^+). Dissociation of these protons occurs stepwise, but in well-separated processes, and the aliphatic amino acids can appear in three different forms in different pH ranges: the cationic (H^2L^+), the neutral or zwitter ionic (HL) and the anionic (L^-) forms.

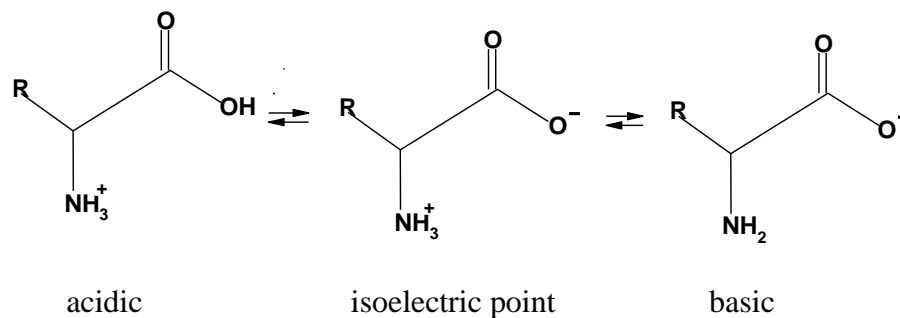


Figure-3: Amino acid dissociation at equilibrium

Amino acids are good metal-complexing agents, forming chelate rings through the amino and carboxylate groups via dissociation of acidic proton as a bidentate N, O-donor (figure-4). These complexes contain 5-membered chelate rings formed via the coordination of amino-N and carboxylate-O donors.

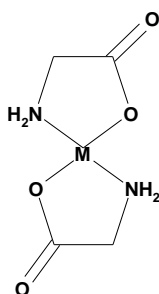


Figure-4: General structural formula proposed for metal-amino acid complexes

The stepwise stability constants ($\log K_1$ and $\log K_2$) of all the octahedral complexes are quite high, suggesting stable reaction intermediate species. The overall stability constants, which are the products of the stepwise stability constants of the octahedral ($K_1 \times K_2$) metal-amino complexes, are very high, revealing good stability (Table-7). This observation was made by L. Antolini [28], the values were found to decrease in the order $K_1 > K_2$, which is expected on the basis of electrostatic concept. The overall stability constant of each complex was determined as the product of the stepwise stability constant; $\beta = K_1 \times K_2$. The number of coordinated amino acid anions to a metal ion determined for nickel is 1:2, which have octahedral geometry. These values are in agreement with the results obtained from similar work carried out by several workers [29-31]. The values of stability constants of investigated Ni(II)-complexes revealed their stability in the following order: $[\text{Ni}(\text{Asp})_2 2\text{H}_2\text{O}] > [\text{Ni}(\text{Gln})_2 2\text{H}_2\text{O}] > [\text{Ni}(\text{Asn})_2 2\text{H}_2\text{O}]$

Table-2

Empirical formula, molecular weight, colour, decomposition temperature and pH of the investigated Ni(II) complexes

Complex	Empirical Molecular formula	formula weight	Colour	Decomposition temperature ($^{\circ}\text{C}$)	p ^H	% Yield
$[\text{Ni}(\text{asn})_2 2\text{H}_2\text{O}]$	$[\text{Ni}(\text{C}_4\text{H}_7\text{N}_2\text{O}_3)_2]$	320.71	Light green	215	7	82
$[\text{Ni}(\text{gln})_2 2\text{H}_2\text{O}]$	$[\text{Ni}(\text{C}_5\text{H}_9\text{N}_2\text{O}_3)_2]$	348.71	Yellowish green	220	6	85
$[\text{Ni}(\text{asp})_2 2\text{H}_2\text{O}]$	$[\text{Ni}(\text{C}_4\text{H}_6\text{NO}_4)_2]$	322.71	Pale green	223	6	89

Table-3*Elemental analytical data, molar conductance and magnetic moments of Ni(II) complexes*

Complex	Elemental analysis Found (Calcd.)				Molar conductance ($\text{ohm}^{-1} \text{cm}^2$ mol^{-1})	μ_{eff} (in BM)
	%M	%C	%H	%N		
[Ni(asn) ₂ 2H ₂ O]	18.31 (18.40)	29.93 (30.01)	4.36 (4.40)	17.46 (17.45)	0.28	3.06
[Ni(gln) ₂ 2H ₂ O]	16.84 (16.90)	34.41 (34.40)	5.16 (5.20)	16.06 (16.05)	0.24	3.08
[Ni(asp) ₂ 2H ₂ O]	18.19 (18.20)	29.75 (29.70)	3.72 (3.70)	8.67 (8.75)	0.25	3.09

Table-4*Important IR bands of the investigated compounds*

Compound	$\nu(\text{O-H})$	$\nu_{\text{s}}(\text{NH}_2)$	$\nu_{\text{s}}(\text{COO}^-)$	$\nu_{\text{asv}}(\text{COO}^-)$	$\nu(\text{M-N})$	$\nu(\text{M-O})$
HAsn	--	3410m	1648m	1585s	--	--
HGln	--	3390s	1645s	1594s	--	--
H ₂ Asp	--	3380w	1650s	1583s	--	--
[Ni(asn) ₂ 2H ₂ O]	3640s	3386m	1390m	1580w	450	340
[Ni(gln) ₂ 2H ₂ O]	3550s	3400m	1410s	1490m	460	315
[Ni(asp) ₂ 2H ₂ O]	3620s	3350s	1445s	1575s	560	310

w= weak; m=medium; s= strong

Table-5*Relevant ¹H-NMR signals for the compounds*

Type of protons	Nature of signal	Chemical shift (δ)
(In Ligands)		
-COOH	singlet	10.95
-CONH ₂	Broad singlet	8
-NH ₂	Broad singlet	6
=CH	quartet	4.2
-CH ₂	pentate	2.1
(In Complexes)		
-COOH	--	--
-CONH ₂	Broad singlet	8
-NH ₂	Broad	6.2
=CH	quartet	4.2
-CH ₂	pentate	2.1

Table-6*Electronic spectral bands and proposed geometry of the Ni(II) complexes*

Compound	nm (ϵ , cm ² , mol ⁻¹)		μ_{eff} (in BM)	Proposed geometry of complexes
	Ligand bands	d-d bands		
HAsn	187, 200, 210	--	--	--
HGln	192, 200, 215	--	--	--
H ₂ Asp	196, 212, 232	--	--	--
[Ni(asn) ₂ 2H ₂ O]	--	526, 472, 452	3.06	<i>O_h</i>
[Ni(gln) ₂ 2H ₂ O]	--	530, 474, 455	3.86	<i>O_h</i>
[Ni(asp) ₂ 2H ₂ O]	--	532, 476, 456	3.89	<i>O_h</i>

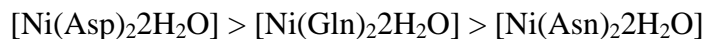
Table-7*Stability constants of investigated Ni(II)-complexes*

Amino acid	Complexes	log K ₁	log K ₂	log β
Asparagine (HAsn)	[Ni(Asn) ₂ 2H ₂ O]	8.64	8.62	17.26
Glutamine (HGln)	[Ni(Gln) ₂ 2H ₂ O]	9.64	9.56	19.20
Aspartic Acid (H ₂ Asp)	[Ni(Asp) ₂ 2H ₂ O]	9.62	9.60	19.22

CONCLUSIONS

Three Nickel (II)-complexes of three α -amino acids: L-Asparagine (L-HAsn), L-Glutamine (L-HGln) and Aspartic acid (L-H₂Asp) respectively were synthesized by easy, efficient, clean, and environmentally benign method. The synthesized complexes were characterized by elemental analysis, conductivity measurements, magnetic moment, and spectral analyses. The elemental data of the investigated complexes revealed their 1:2 (metal to ligand) stoichiometries and monomeric nature and lower molar conductance values show the non-electrolytic nature of the complexes. The infrared spectral studies revealed the monobasic bidentate (N & O donor) nature of the amino acid ligands which coordinated through amino-N and carboxylate-O with Ni²⁺ ion in the complexes. The magnetic moment values and electronic spectral studied indicated the octahedral geometry of the investigated complexes. These complexes contain 5-membered chelate rings formed via the coordination of amino-N and carboxylate-O donors. The overall stability constants, which are the products of the stepwise

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Conflicts of interest

The authors declare no conflict of interest.

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