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IR charactizations, TGA analysis and thermodynamic parameters of some metals– Tryptophan complexes

Hamad M Adress Hasan[1], Fatimah A Abdulsayid[2], Hanibal A Khatab[1]
[1] Chemistry Department, Faculty of Science, Omar Al–Mukhtar University, Albaydha, Libya
[2] Chemistry Department, Faculty of Science, Benghazi University, Alkufra, Libya

Abstract
This study was conducted to prepare some complexes by using Tryptophan as a ligand with some metal chlorides including (Cadmium, Zinc, Nickel, Copper, Chromium, and Cobalt). The resulting combinations have been demonstrated by using infrared analysis (IR) and thermodynamic analysis (TGA) Also some of physical properties such as electrical conductivity, complex color and melting point were estimated for each complex. The potentiometric studies were carried out to estimate the thermodynamic parameters and ionization and stability constants.

Keywords: complexes, IR, potentiometric, thermogravimetric analysis, tryptophan

Introduction

Amino acids have both a basic amino group and an acidic carboxyl group. The ability of amino acids to bind together in long chains by forming amide bands between the NH_2 of one amino acid and the -COOH of another gives them their importance as biological building blocks [1]. The amino acid can coordinate through several different boding interactions, according to structural studies of a wide variety of transition metal amino acid complexes. The ligands contain two distinct types of potential donor centres (S or – NH2 and –COOH), which are based on the metal ion, its oxidation state, and the primary structure of the amino acid [2]. New complexes of some transition metal ions [Co(II), Ni(II), Cu(II)] and some non-transition metal ions [Zn(II), Cd(II)] with a number of Schiff bases obtained from the condensation of some amino acids (Methionine) and (3-acetyl pyridine, 4-acetyl pyridine, acetoacetaanilide) have been prepared. Elemental analysis, molar conductance, magnetic susceptibility infrared, and electronic spectral analysis were used to classify all of the prepared complexes [3]. Potentiometric titration in aqueous solution was used to establish the dissociation constant, pKa, of proline, threonine, and asparagines. Extrapolations revealed that the pKa of proline, threonine, and asparagines are 10.54, 10.31, and 9.39, respectively. Potentiometric titration in aqueous solution was also used to evaluate the overall stability constant of the corresponding nickel (II) complexes. In all of the complexes, there were three coordinated amino acids to the nickel (II) ion [4]. At pH = 7.30 0.01, and = 1.0 M NaClO4, voltametric reduction of Zn (II) using (L-lysine, L-ornithine, L-threonine, L-serine, Lphenylglycine, L-phenylalanine, L-glutamic acid, L-aspartic acid, and vitamin-PP, nicotinamide, niacinamide) was recorded at 25 and 35 ºC. The thermodynamic parameters such as enthalpy (ΔH), free energy (ΔG) and entropy change (ΔS) have also been reported [5]. Potentiometric studies of complexes produced by the chromium (III) ion and amino acids were conducted. The amino acid dissociation constants, stepwise formation constants, and overall stability constants of metal ions and amino acid complexes have all been determined. The overall stability constants of the complexes obtained are relatively large, suggesting that the complexes are stable [6]. The main aims of the study are using modified and simple method to synthesis complexes by using tryptophan as a ligands and some metal chlorides. Then identification the obtained complexes by different analysis methods (IR and TGA) beside determination the pka values of the complexes by potentiometric calculations in addition to estimate the thermodynamic parameters.

Experimental Part

Chemical Compounds: All the chemicals used in this study were laboratory-grade. $CrCl_3.3H_2O$, $CuCl_2.2H_2O$, $CoCl_2H_2O$, $CdCl_2.4H_2O$, $ZnCl_2.4H_2O$, $NiCl_2.H_2O$ tryptophan, NH_4, NaOH, HCl, NaCl, and distilled water.

Ligand: In this study Tryptophan was used as a ligand.

Synthesis of metal–L-Tryptophan– complexes: 0.8 mole of metal chloride in 50 ml ammonia was added with stirring to 0.6 mole of Tryptophan ligand in 50 ml distilled water. The reaction mixture was refluxed and then left overnight. The precipitated solid complexes were separated out by filtration, then washed with water and dried over P_2O_5.

Characterization of the synthesized complexes

Conductivity: A conducto meter was used to calculate the conductivity of the complexes' solutions (Type HANA).

Melting point: It was determined by the use of machines of various types (Melting point Apparatus SMP3).

Determination of metal complexes: 0.02 g of the solid complex was digested in 5 ml of concentrated nitric acid and dried almost fully. All metal ions were measured using atomic absorption after the residue was dissolved in water (Central lab of higher institute of aquatic research, Alexandria, Egypt).

Infrared spectra: The infrared spectra of the ligands and their metal complexes were taken in potassium bromide discs using the I.R-spectrophotometer covering the range from 200 to 4000 cm^{-1}.

Thermogravimetric analysis

The thermogravimetric analysis of some amino acids complexes which contain water molecules was achieved by using thermal technique model TGA-H50 Shimadzu (Japan). The weight loss of (1.33-16.85) mg sample was measured from room temperature up to (1000ºc) in rate of 10 °C per min.

Potentiometric determination of the ionization constants of the ligands and the stability constants of their metal chelates

The applied method

The ionization constants of the ionizable groups are determined potentiometrically [using Jenway, pH-meter 3310] applying Sarin and Munshi technique which involve preparation of the three mixtures:

a. 5 ml of standard 0.01M HCl + 5 ml of 1M NaCl + 15 ml ethanol.
b. 5 ml of 0.01M HCl + 5 ml of 1M NaCl + 15 ml of ethanol + 0.5 ml of 0.1M ligand.
c. 5 ml of 0.01M HCl + 5 ml of 1M NaCl + 15 ml of ethanol + 0.5 ml of 0.1 M Ligand + 0.5 ml of 0.1 M metal chloride.

Each one of the above three mixtures were titrated potentiometrically against standard sodium hydroxide solution (0.05M) using pH – meter at a particular temperature and ionic strength. The values of pH were recorded after each addition of NaOH. The relation between pH and volume of NaOH added was drawn for each mixture.

The three titration curves obtained are referred to as:

(a) acid titration curve, (b) ligand titration curve, (c) complex titration curve.

The three titration curves (a, b and c) were plotted for each chelate.

Determination of thermodynamic parameters

The following thermodynamic parameters: ΔG°, ΔH° and ΔS° were determined for each chelate depending on their stability constants. The free energy of formation (ΔG°) of a complex is related to its stability constant by the relation

$$-\Delta G^{\circ} = -2.303\ RT \log\beta$$

R = universal gas constant, T = absolute temperature, logβ = stability constant of the complex

Enthalpy of formation (ΔH°) and entropy (ΔS°) were calculated by plotting logβ versus 1/T.

We can specify the quantitative dependence of the stability

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$$

$$\Delta G^{\circ} = -2.303\ RT \log\beta = \Delta H^{\circ} - T\Delta S^{\circ}$$

we can rearrange this equation to give

$$\log \beta = -\Delta H^{\circ}/(2.303\ RT) + \Delta S^{\circ}/(2.303\ R)$$

Note that this is a linear equation of the form y = mx + b, where y = logβ, m = $-\Delta H^{\circ}/(2.303\ R)$ = slope, x = 1/T, and b = $\Delta S^{\circ}/(2.303R)$ = intercept. This means that if the values of K for a given reaction are determined at various temperature, a plot of logβ versus 1/T will be linear, with slope $-\Delta H^{\circ}/(2.303R)$ and intercept $\Delta S^{\circ}/(2.303R)$. This result assumes that both ΔH° and ΔS° are independent of temperature over the temperature range considered. This assumption is a good approximation over a relatively small temperature range.

Results and discussion

Characterization of the prepared complexes

Table 1: Shows the colours, concentrations of the metals and the electrical conductivity of the complexes

Complexes	Parameter		
	Colour	E.C	Metal content (ppm)
Try –Cd	Yellow	2.08	0.14
Tyr – Cr	Green	1.33	0.004
Try –Zn	White	1.07	0.081
Try – Cu	Light blue	0.76	0.004
Try -Ni	Green	1.44	0.029
Try – Co	Pink	1.79	0.008

Electrical conductivity

Table (1) shows the E.C in non-aqueous solution which were carried out to help in characterizing the structure of the complexes under investigation. The results were ranged between (0.76 -2.08), supports the presence of non – electrolyte nature for these complexes, also these values indicated that no anions existed outside the coordination sphere.

Infrared spectra studies

The following is shown by comparing the IR spectra of the ligand and its metal complexes:

1. N-H and N-H and C=O are the tryptophan bands located at 3399 cm^{-1}, 2959 cm^{-1}, and 1580 cm^{-1}, respectively[7]. The first band of the free ligand is shifted to higher frequency in case of the most complexes (Cd, Cr, Cu and Ni). On the other hand, The N-H ligand band is subjected to changes in position in the Cd, Zn, Cr, and Cu complexes but completely disappeared in case of the Ni complexes. From these results can come to a conclusion that the amino group is of major importance for coordination in most of the studied complexes.
2. The ligand gave two infrared spectral bands in the vicinity of 1658 cm^{-1} and 1409 cm^{-1} attributable to the asymmetric and symmetric vibrations of the carboxyl groups [8]. The band at 1409 cm^{-1} is slightly shifted in case of Cd, Cr and Co complexes and shifted to lower frequency, but still existing in the same position in case of the Zn complex and becomes of broad nature in case of Ni complex Such finding suggests that the carboxyl group takes part in the cobalt complex through deprotonation [9]. It was reported that the metal- oxide. Stretching frequencies lie within the range 700 - 500 cm^{-1}. In most of the metal complexes possible coupling can occur. This can be attributed to $\gamma_{(M-O)}$ ring

deformation. In many instances two bands are observed: one of medium to strong intensity and a weaker band at frequency 10 - 40 cm $^{-1}$ lower than the stronger band. However, the frequency of $\gamma_{(M-O)}$ is not very sensitive to the atomic mass of M [10]. The nitrogen atom tends to lower the solubility of the complexes in non- solvents. So the complexes of oxygen-nitrogen ligands are in general, either sparingly soluble or insoluble in non-polar solvents. From the sparse data available, oxygen-nitrogen ligands appear to give rise to a smaller reduction, in theinter electronic repulsion energy than oxygen - oxygen Ligands. This presumably is due to that the nitrogen atom having a low position compared to some donor atom in the nephelauxetic series [11]. Also, the metal-nitrogen stretching frequencies can occur over a wide range, viz. from 600 to below.

3. The band Located at 988 cm-^{1} in the free ligand could be assigned to diametric structure, Such band is shifted in the most prepared complexes, but absent in case of Ni and Co complexes. Based on I.R data from the fundamental groups (N–H, NH_2, and COOH), as well as data from electronic measurements gathered during elemental analysis the following structure of the prepared complexes could be suggested:

Table 2: Fundamental infrared band (cm^{-1}) for the prepared tryptophan complexes

Complex	OH(H_2O)	NH_2	C = O	M -O
Try –Cd	3400	3009	1407	736
Tyr – Cr	3400	3009	1408	766
Try –Zn	3398	3010	1409	737
Try – Cu	3406	3252	1431	762
Try -Ni	3401	-	1400	739
Try – Co	3394	-	1390	739

Thermogravimetric Analysis (TGA)

The thermogravimetric analysis curves allowed us to establish the temperature below which the characterized compound has a constant weight and which begins to decompose and how far the decomposition reaction can proceed [12]. The observed and stoichiometric decreases in weight of the substance make it possible to estimate an intermediate product which is formed during decomposition and at what temperature occasionally the temperature rang where this intermediate has constant weight [13]. The thermogravimetric analysis data for some tryptophan complexes are given in Table (3). The weight loss of Tr Ni, Tr Cu and Tr Cr complexes corresponding to loss of water molecules at the temperature range of (189 to 259.3 ˚C). And the loss of CO_2 molecules were occurs at the temperature range (435.7 to 496.3)[14]. While the residual of metals oxides (MO_2) of (704.96 - 987 ˚C) rang was appeared.

Table 3: The thermogravimetric analysis data for tryptophan complexes

Complex	Decomposition		
	H_2O Temp. rang	CO_2 Temp.	MO_2 Temp.
Tr - Ni	RT-232.6	468.4	822
Tr - Cu	RT-259.3	435.70	704
Tr - Cr	RT-189.1	496.3	987

In general the steps of the investigated complexes may be occurred as:
$[ML.nH_2O].nH2O \rightarrow [ML.nH_2O]$
$[ML.nH_2O] \rightarrow [ML]$
$[ML] \rightarrow$ intermediate (unstable)
Intermediate $\rightarrow$ Metal oxide MO_2
Intermediate (decomposition of organic ligand).

Potentiometric studies of the ligands and their complexes

The experimental techniques used for this purpose is potentiometric titration. This technique is useful in establishing the nature and stoichiometry of the complexes formed in solutions.

Determination of the ionization constants of the ligands and the stability constants of their complexes

In this case the following three solutions have been prepared:

a. A solution containing the mineral acid alone.
b. A solution containing the mineral acid and the ligand only.
c. A solution containing the mineral acid, ligand and metal ion.

Each one of the above three solutions was titrated with standard sodium hydroxide solution and are referred to as curves a, b and c, respectively. The experimental results so obtained at various temperatures (25 °C, ***35*** °C), he titration curves of the all ligands and metal ions studied are given in Figures (1-6).

The ionization constants (pK_a) of the ionizable groups in the investigated ligands of amino acid were determined by applying the potentiometric technique described by[15] using titration curves (a) and (b). Inspection of the titration curves for the ligands (curve b) shows that these are characterized by the presence of one sharp jump indicative of one neutralization equilibrium for each ligand. The stability constants of the following metal ions (studied metals) complexes with amino acids using the method described by [15]. The stability constant for each complex was determined at two different temperatures (25, 35 ˚C), in order to determine the thermodynamic parameters for each complex.

Referring to the titration curves it can be found that the complex titration curve is separated from ligand titration curve, the end points of the titration of the three mixtures increase in the order a < b < c. The potentiometric curves are almost S-shaped.(Figure 4).

All calculations in this research were carried out by "Microsoft Excel" program, and the curves were obtained using "Origin" program.

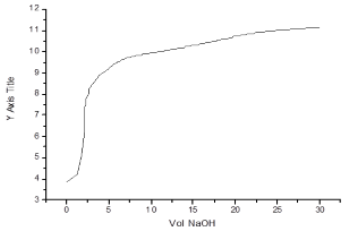

Figure (1) : pH – titration curve of Cd complex

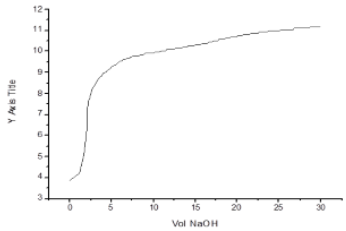

Figure (2): pH – titration curve of Cr –tr complex.

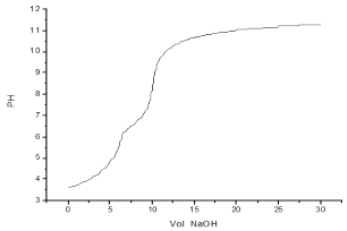

Figure (3) : pH – titration curve of Zn complex

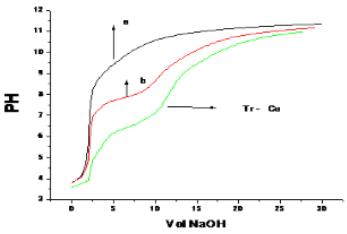

Figure (4): PH–Titration curves of acid, ligand and Cu complex.

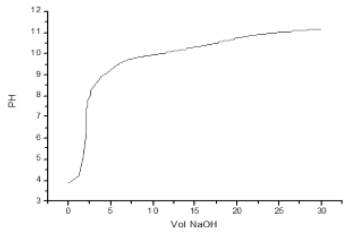

Figure (5): pH – titration curve of Ni complex.

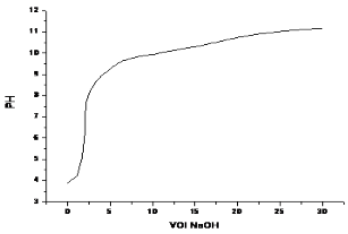

Figure (6) : pH – titration curve of Co complex

Fig

Thermodynamic parameters of ionization:

The behaviour of such compounds at different temperatures was investigated in the temperature range 25-30 ˚C. The data are represented in (Figure 7) and (Table 4). One can come to the following observations and conclusions:

The pka values of Tryptophan ligands decrease with increasing temperature.

The familiar equation: $K= A e^{-\Delta E/RT}$.

Is applied for studying the effect of temperature on the pk values. On formulating this equation in pk function: pk= (ΔH/2.303RT) + Const.

On plotting the pk (log β) values versus 1/T, straight lines are obtained with a slope amounting to ΔH/2.30, from which the ΔH values, (K.Cal /mole) can be computed (Table 4).

1- The free energy values, ΔG (K.cal/mole) are calculated based on the equation:

ΔG= 2.303 RT pk

2- The ΔS values are achieved based on the relation: ΔG= ΔH – TΔS.

Table (4), interesting observation can be made. In case of the ligands under investigation, the ΔS values are of negative sign. such finding goes parallel to those reported for ligands containing amino acids through intermolecular hydrogen bonding.

Table 4: Thermodynamic parameters of ionization of the amino acids

Compound		Pk (log β)		ΔG at 25ºC (KJ/mol)	ΔG at 35ºC (KJ/mol)	ΔH (KJ/mol)	ΔS (KJ/mK)
		25ºC	35ºC				
Tryptophan	pk_1	8.27	8.23	47.196	48.587	5.7	-139.09
	pk_2	7.49	7.38	44.184	42.137	18.868	-240.17

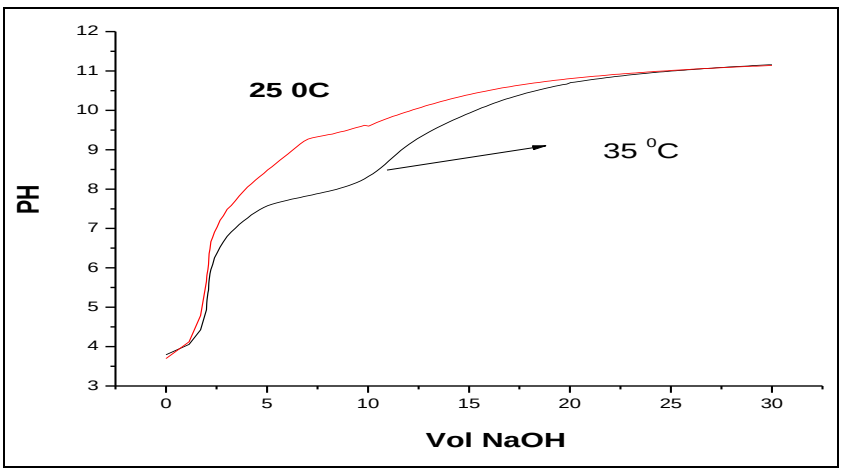

Fig 7: pH-titration curves of Tryptophan at different temperatures comments on the pka values

Two pka values were obtained potentiometrically for Tryptophan, the PKa results summarized as follow: Potentiometrically, the two pka are equal 8.27 and 7.49, this is attributed to the deprotonation of the carboxylic group.

The values of ΔG and ΔH were positive indicated that the reaction between metal and ligand is nonspontaneously and enothermic.

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