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Original Research Article

Synthesis, Characterization, and Antibacterial Studies of Metal Complexes with Tyrosine Ligand

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ABSTRACT

In this study, Zinc(II) , Mn(II), Hg(II), and Tin(II) complexes of were synthesized and characterized via Infrared spectroscopy (IR), thermal analysis (TGA), measurement of melting point and molar conductivity. The results provide evidence of coordination of the metal ions to Tyrosine ligands through NH2, and COOH a groups with proposed octahedral geometry, low spin, paramagnetic. The TGA curves were gave one of the main decomposition of complexes, and stable at M- oxides. The molar ratio which carried out by U.V calculations gave the ratio of 1:1 (Metal : Ligand) linkage. Their antibacterial activities were investigated using ultraviolet light for molar ratios calculations with items by using the different series of concentrations and Ligand. Study of the effect of complexes prepared on some bacteria (Escherichia coli and Bacillus Subtitles) has enriched the two types of bacteria with the complexes prepared on each species of microbial laboratory. The prepared complexes gave anti-bacterial activities on the species of bacteria which used in this study.

Keywords: Tyrosine ligand, spectroscopy investigation, Metal complexes, anti-bacterial activities .

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Introduction

In bioinorganic chemistry, metal complexes have been used for the treatment of many diseases such as cancer, arthritis, diabetes, and Alzheimer's.1,2. Metal complexes using amino acid are a large family of coordination complexes containing the conjugate bases of the amino acids, the 2-aminocarboxylates. Amino acids are prevalent in nature, and all of them function as ligands toward the transition metals [1]. The important of metal complexes with amino acids come from their biological applications. Metal amino acid complexes are similar to these compounds which allow the metal to be carried in with the amino acids during absorption and can be used to build proteins or provide energy [2]. Complexes of Cu (II) with amino acids can be used as models to study the pharmacodynamics effects of drugs or for increasing the biocompatibility and minimize toxic effects of some metal . Metalloid therapy is a very unique therapeutic method to treat many diseases. Several metal ions and their complexes exhibit anti-diabetic effects [3]. Amino acid coordinates to metals it confirms structural liability , and also have applicability in enzyme inhibition. These complexes have a vast area in pharmacological and toxicological properties that has drawn lot of current attention [4]. Metal complexes with amino acids have received much attention because they proved to be useful antibacterial agents applied against Staphylococcus aurous, Escherichia coli, nutritive supplies for humans and animals [5]. The importance and applications of metal complexes are widespread from synthetic chemistry to material science and biochemistry. These metals have been used for drug design and delivery[6]. Hemoglobin is most important oxygen

transport metalloproteinase which contain iron metal in body. Transferrin and ferritin proteins also contain iron which transports it from one part of the body to another, providing storage. The diets containing iron from amino acids complexes have better metabolism, absorption as well placental and mammary iron transfer than any other form. Ferrous bis-glycinate complex nutritionally meets all the requirements [7].

Materials and Methods

Solutions

Tyrosine is the amino acid which used as ligand in the concentrations of (0.2M).

Synthesis of the metal complexes:

Synthesis of Tyrosine –metal complexes:

(0.01 M) of metal chloride in 50 ml ammonia was added with stirring to (0.01 M) of Tyrosine 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 at room temperature.

Characterization of the synthesized complexes

Melting Point measurement :

The melting points of both ligands and their complexes were measured using a device (Stuart Melting Point Apparatus.

Table1. Chemicals used in this work.

Chemical Materials	Formula
Mercury(II) Chloride	$HgCl_2$
Zinc(II) Bromide	$ZnBr_2$
Tin(II) Chloride -2-hydrate	$SnCl_2.2H_2O$
Manganese(II) Chloride	$MnCl_2$
Ammonia	NH_3
Distilled water	H_2O
Tyrosine	$C_9H_{11}NO_3$

Determination of conductivity:

The conductivity of the solutions of the complexes was measured using conduct meter (Type HANA) .

Infrared spectra:

The FT-IR spectra of the metal complexes were recorded for potassium bromide (KBr) discs over the range 4000-400 cm^{-1}. On the basis of the reported infrared spectra of amino acids, Tyrosine ligand and their metal complexes. An instrument based on the fundamental principles

of molecular spectroscopy was utilized in order to identify the presence of certain functional groups in the synthesized compounds.

Thermo- Gravimetric Analysis:

Thermo- Gravimetric Analysis (TGA) is an analytical technique used to characterize the materials by measuring the amount and rate of weight change of a substance as a function of temperature or time in a controlled atmosphere. With this analytical technique, the fraction of volatile components in a compound can be identified by measuring the changes in the sample weight. The temperature is most often programmed to increase linearly. The thermo-gravimetric 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 sample was measured from room temperature up to (1000 ^{o}C) in rate of 10 ^{o}C per min [8].

Determination of the molar ratio:

The molar ratio of the metal ions to the ligands was determined spectroscopically. The spectrophotometric method was used in this investigation to determine the stoichiometry of the complexes. Spectrophotometric method can be carried out by: molar – ratio method. In this method, [10] volumetric flasks (10 ml) were cleaned, 2 ml of $3x10^{-3}$ M of the ligand was transferred inside each flask, the flasks were numbered from 1 to 10, then 0.4 ml of $1x10^{-3}$ M metal salt aqueous solution was added to the first flask, 0.8 ml to the second, 1.2 ml to the third, each flask has 0.4 ml of metal solution more than the previous one, and so on until 4.0 ml was added to the tenth flask. The volume in each flask was made up to the mark (10 ml). A series of [L]/[M] ratios were obtained. Using UV spectrophotometer, the absorption of each solution was measured at maximum wave length (λ max) of the expected complexes. The absorbance values were plotted against [L]/[M] ratios. The result curves are composed of straight lines with inflection points, [L]/[M] ratio corresponding to the infection point indicates to the actual stoichiometry of the complex. This procedure was repeated for each metal complex, all of the investigated ligands were titrated with the metal ions (Mn, Zn, Sn and Hg).

The biological study:

In this study two groups of bacteria were testing for the metal complexes with tyrosine ligand, Gram-positive bacteria (Bacillus) and Gram-negative bacteria (Escherichia colli).

Results and Discussion

Characterization of the prepared complexes

Table 2. shows the colors, melting point and the electrical conductivity of the complexes

Parameter / Complex	Colour	E.C(µS/cm)	M.P (℃)
Tyr-Hg	beige	4.77	233
Tyr-Zn	Milk white	3.56	>350
Tyr-Sn	Light yellow	6.13	324
Tyr-Mn	Light brown	4.75	289-291

Infrared spectra studies

Table 3. shows the fundamental infrared bands (cm^{-1}) for the prepared tyrosine metal complexes.

Complex	OH (phenolic)	NH_2	C = O	M -O
HgL	3180	3031	1581	651
ZnL	3356	3243	1643	573
SnL	3200	3100	1582	601
MnL	3199	3098	1582	550

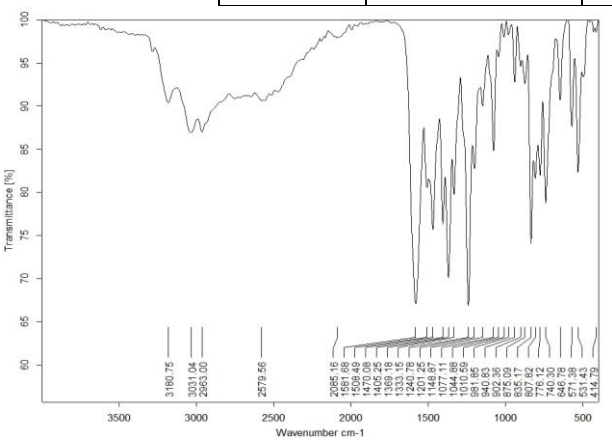


Fig.1: The infrared spectra of complex [Hg-L].

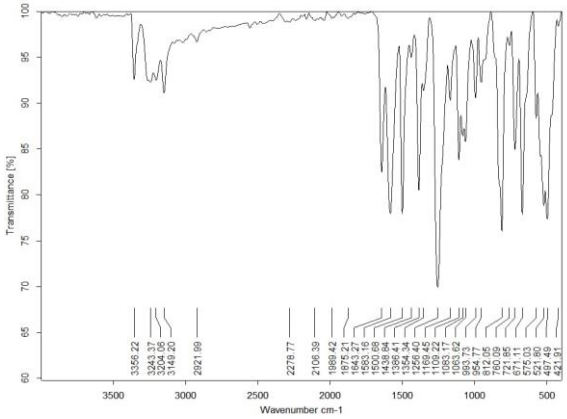


Fig.2: The infrared spectra of complex [Zn-L]

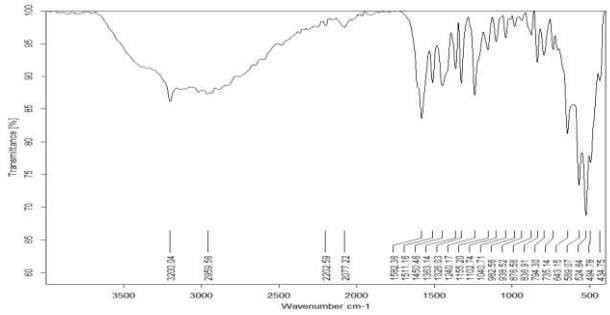


Fig.3: The infrared spectra of complex [Sn-L].

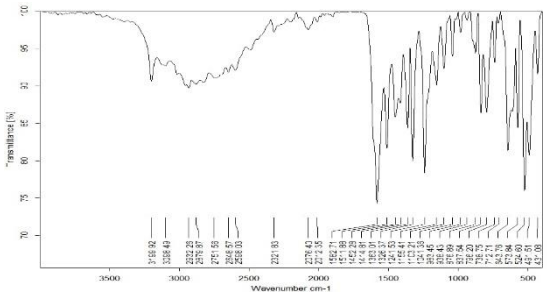


Fig.4: The infrared spectra of complex.

Thermo-gravimetric analysis (TGA)

Table 4. Shows the thermo-gravimetric analysis data for tyrosine complexes.

Decomposition / Complex	H_2O Temp. rang	CO_2 Temp.	MO_2 Temp.
Tyr - Hg	RT-251	301	426
Tyr - Zn	RT-401	503	580
Tyr - Sn	RT-307	490	980
Tyr - Mn	RT-375	510	830

In general, the steps of the investigated complexes may be occurred as:

$[ML.nH_2O].nH_2O \rightarrow [ML.nH_2O]$

[ML.nH2O] → [ML]

[ML] → Intermediate (unstable)

Intermediate → Metal oxide MO_2 Intermediate (decomposition of organic ligand).

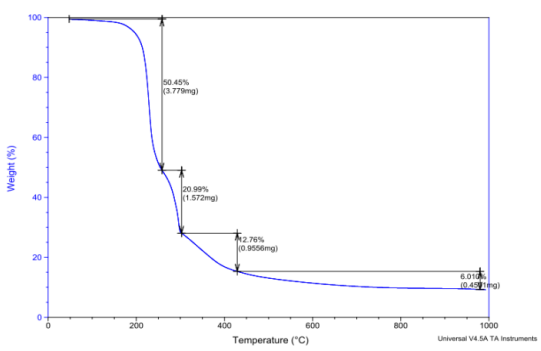


Fig.5: The TGA curve of Hg complex.

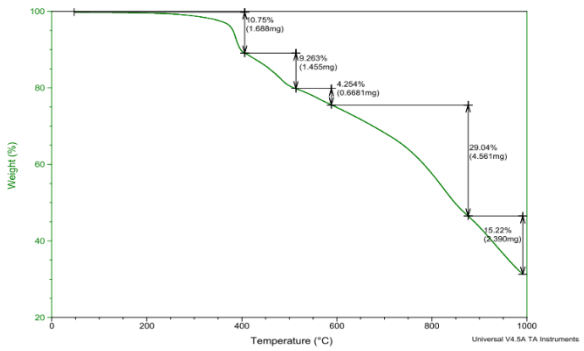
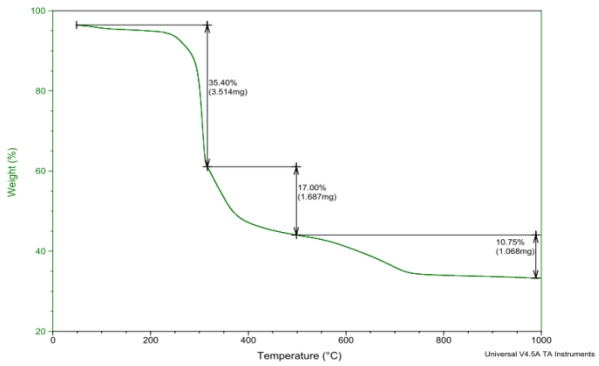


Fig.6: The TGA curve of Zn complex



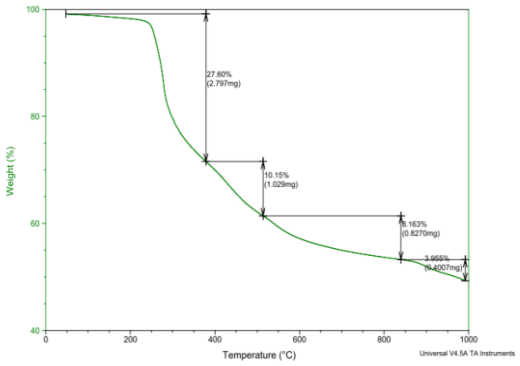


Fig.7: The TGA curve of Sn complex. **Fig.8:** The TGA curve of Mn complex

Spectrophotometric Studies

In this investigation, the concentrations of the metal ions were varied and the ligand concentration were maintained constant, so, a series of metal–ligand aqueous solutions were prepared with different [L]/[M] ratios. The absorptions of these solutions were measured using UV spectrophotometer at λ_{max} of the expected complex MLx. Absorbance versus [L]/[M] curves were drawn for all complexes. It was observed that the absorption increase linearly as the metal ion concentration increase, because of the formation of the complex, until the solution reaches the actual molar ratio of the investigated complex. At this point, all of the added materials were completely reacted, and the absorption observed is the absorption of the investigated complex alone. After this point, the excess amount of the added metal ion causes an inflection in the straight line, that is because the metal ion has an absorption value differ from that of the complex at λ_{max} of the complex. [L]/[M] ratio corresponding to the inflection point in (ABS - [L]/[M] curve) indicates to the actual [L]/[M] ratio of the investigated complex, Referring to the Figure 9, it was found that of the Tyrosine metal complexes in this investigation are able to be stable in the form ML.

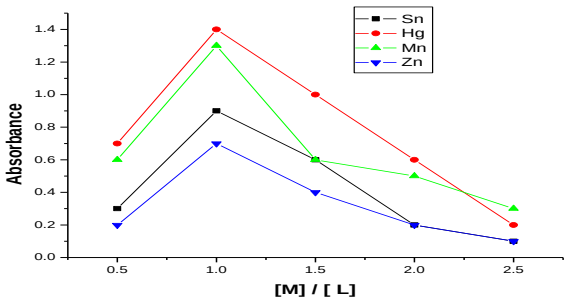
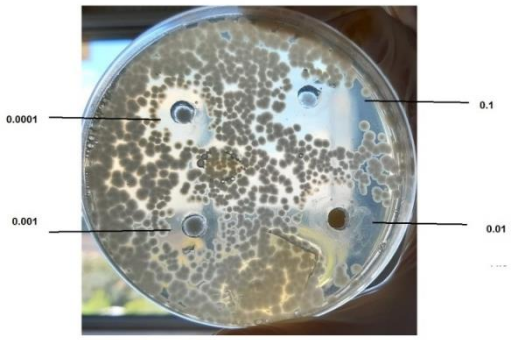


Fig.9: The relationship between molar ratio of ligand- Absorbance of the metal ions of (Sn, Hg,Mn and Zn).

The biological activity of complexes with bacteria

Table5. The inhibition zones in millimeter of the ligands and their Complexes.

	Bacillus				*E.colli*			
	Concentration(mglml)							
Complexes	0.1	0.01	0.001	0.0001	0.1	0.01	0.001	0.0001
$[Hg(Tyr)_2]$	10	8	7	6	8	6	3	-
$[Zn(Tyr)_2]$	-	-	-	-	-	-	-	-
$[Sn(Tyr)_2]$	-	-	-	-	-	-	-	-
$[Mn(Tyr)_2]$	-	-	-	-	-	-	-	-



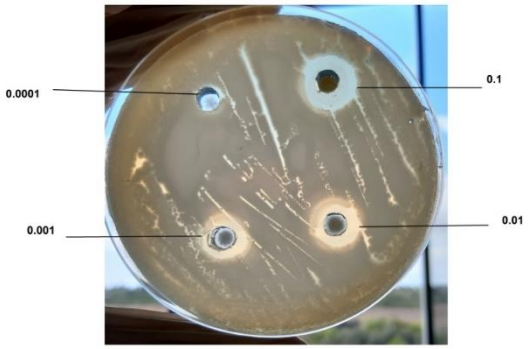


Fig.10: Biological activity of the [Hg(Tyr)] **Fig.11:** Biological activity of the complex with the (Bacillus) bacteria complex with the (E.coli) bacteria.

Conclusion

From the obtained data recorded in this study, the reactions between the Tyrosine ligand with selected metals ions of (Mn , Zn , Hg and Sn) is rapid , simple and sensitive to product complexes which gave interesting results of I.R , U.V and TGA. Also the complexes gave activities of the studied species of Bacteria.

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