International Journal of Chemical and Biological Sciences
www.chemicaljournal.org
Online ISSN: 2664-6773, Print ISSN: 2664-6765
Received: 22-05-2021; Accepted: 04-06-2021; Published: 23-06-2021
Volume 3, Issue 1, 2021, Page No. 09-14

Synthesis, characterization of some tryptophan complexes and their biological studies on root knot nematode

Fatimah A Abdulsayid[1], Younis A Bader[2], Hamad M Adress Hasan[3]
[1] Department of Chemistry, Faculty of Science, Benghazi University, Alkufra, Libya
[2] Department of Botany, Faculty of Science, Benghazi University, Alkufra, Libya
[3] Department of Chemistry, Faculty of Science, Omar Al–Mukhtar University, El–Beida, Libya

Abstract
Some of metal complexes were prepared by modified and simple reactions between Tryptophan (as ligand) with some metal ions of: Zn (II), Fe (III) and Cu (II). The complexes were investigated using several physical techniques as: molar conductance measurements, colour and melting point in addition to the infrared investigation spectra. The thermogravimetric analysis TGA was performed for the Complexes. The biological activity on effect of three complexes on egg hatching and mortality in RKN second-stage juveniles were studied.

Keywords: tryptophan, complexes, IR, TG, root knot nematodes (RKN)

Introduction

Root knot nematodes (RKN) are a type of plant parasitic nematode that belongs to the Meloidogyne genus. RKN larvae infect plant roots, causing the development of root knot galls infection of young plants may be lethal [1]. Meloidogyne parasites hatch from eggs as vermiform, second-stage juveniles (J_2), the first moult having occurred within the egg. J_2s larvae do not feed during the free living stage, but use lipids stored in the gut, and J_2 larvae are danger stage on root plant [2].

Amino acids are organic molecules that have both an amino group (NH_2) and a carboxylic acid group (COOH) bound to the same carbon atom. Amino acids of this kind are also known as α – amino acids. Thus an α – amino acid is made up of an amino group (- NH_2), a carboxylic group (- COOH), a hydrogen atom (H), and a unique R – group bound to α – amino carbon atom. Amino acids have been shown in the literature to form complexes with transition metals on numerous occasions [3].

Tryptophan is a form of important amino acid found in the bodies of humans and herbivores, and it is one of the precursors of catecholamines including dopamine and serotonin 1, 2. The brain serotonin availability depends upon blood TrpH levels, which could modulate the psychoneural regulation of spontaneous alternation through presynaptic inhibition of hippocampal cholinergic terminals. Therefore, TrpH is an essential component of proteins and is needed for the establishment and maintenance of a positive nitrogen balance in humans [4, 5].

The manufactured new complexes were characterized by IR, color, and melting point determination for some of the complexes prepared by reaction between Schiff base (3-methoxy-4-hydroxy-benzaldehyde with Valine) and different biological applications were applied on the synthesized Complexes [6]. CHNS elemental tests, molar conductance, magnetic moment measurements, infrared and electronic spectroscopies were used to investigate three new 1,3-bis(2-hydroxybenzylidene)thiourea complexes. The electron paramagnetic resonance spectrum of the Cr (III) complex was measured. For [TiO.H_2O], a thermogravimetric analysis (TG) was performed. The hydrated and coordinated water molecules present in the 10H_2O complex are established [7]. The aim of this study is to prepare Zn (II), Fe (III), and Cu (II) complexes with L-Tryptophan and investigation their geometrical structures by using IR spectra, thermal gravimetric analysis (TGA), and some physical properties to characterize the prepared methods including (Color, electrical conductivity and melting points), as well as the effect of the prepared complexes on egg hatching and mortality in RKN second-stage juveniles.

Experimental part

Materials

All of the chemicals used in this study were reagent grade. L-Tryptophan was used as a ligand, and metal salts such as Zn $(NO_3)_2.3H_2O$, Fe $(NO_3)_3$, and Cu $(NO_3)_3$ were used to complex with L-Tryptophan, some solvents were used in this including, ethanol (C_2H_5OH), sodium hydroxide (NaOH), ammonium solution. Double distilled water were used throughout the experiment.

Ligand

L-Tryptophan the amino acid which used as ligand.

Preparation of complexes

The complexes under investigation were prepared by mixing 25 cm^3 ammonium solution of the Tryptophan (0.02 moles; 4.08 g) with the same amount of ammonium solution of the metal salts (0.02 Mole); $Zn(NO_3)_2.3H_2O$ (4.86g), $Fe(NO_3)_3$ (2.32g) and $Cu(NO_3)_2.3H_2O$ (4.82g). The obtained mixtures were refluxed with stirring for 1.5 hours, the mixture leaving in darkened place even of two day. The obtained products were filtered, and dried in desiccators over anhydrous $CaCl_2$ under vacuum. The yield

ranged from 60-75% and the melting points of all complexes are above 350 ^{0}C.

Measurements

The conductivity values of the prepared complexes were measured by using (conduct meter) type HANA Conductometer at central Lab of faculty of Science, Omar El –Mukhtar University. The melting point was measured by using machines type (Melting point Apparatus SMP3). The infrared spectra of the Ligand and their metal complexes were taken in KBr discs using the IR (Type thermo FT-IR 380 Nicolet Company) spectrophotometer covering the range from 500 to 4000 cm^{-1}. The thermo gravimetric analysis (TGA) of some amino acids complexes which contain water molecules was achieved by using thermal technique model TGA-H50 shimadzu (Japan), the weight lost of sample was measured from room temperature up to (1000 C^o) in rate of 10 C^o per min, at Alexandria University, Alexandria - Egypt.

Biological applications test

A laboratory experiment was conducted at 24±2 ^{0}C. Egg masses and J_2s of RKN, placed in Petri dishes filed with 5 ml tap water, were subjected to three doses, 0.01, 0.05 and 0.09 mg of complexes. The three doses were selected based on previously published articles and our preliminary test [8]. Egg masses in water alone served as controls and 100 J_2s in water alone served as controls. Each replicate of egg hatching consisted of 5 egg masses/Petri dish, and each replicate of mortality J_2s consisted of 100 J_2s/Petri dish. The Petri dishes were examined after 3 day under a dissecting microscope (Nikon Japan) and the number of hatched J_2s of RKN was counted and the number of live and dead J_2s of RKN was counted.

Results and Discussion

The physical properties of the L-Tryptophan and its complexes.

Table (1) gives the color, melting point and molar conductivity of the L-Tryptophan as Ligand and its complexes.

Table 1: physical properties and molar conductance of the complexes.

Complexes	Color	M.p (C^0)	E.C(µS)
L-Tryptpphan Ligand	White	290	7.3
Zn(II) complex	White	< 350	0.23
Fe(III) complex	Light brown	< 350	0.17
Cu(II) complex	Dark blue	< 350	0.20

The Colour

Tables (1) showed that the color of the ligand changed from white to several different colors depending on the type of metal, with this change owing to the influence of the Ligand's linkage and the different electrons in 3d orbitals [9]. The difference in energy between the two states energy in the atom during the attracting between the ligand and the metal of electrons in 3d orbital and portioning them for groups the high and low in energy is proportional to the magnetic frequency beam. A high energy level is reached by certain electrons. The color of the complex was determined by the number of electrons in orbital d for metal and nature ligand whenever the difference in energy between the two groups 3d was increased, as well as the atom's ability to absorb several frequencies from the beam [10].

Melting Point

The melting points of the studied complexes showed differences between the free ligand and complexes, which was due to the bounded between the metals and the ligand [6].

Electric Conductivity

The E.C. values in most of the complexes studied were low, ranging from 0.17 to 0.23 µS. The conductivity of complexes was stated to be dependent on free electrons not in conjugation in the last orbitals, with conductivity decreasing when conjugation occurs between the metal and the ligand, which could mean that these electrons are bounded [11].

IR spectra studies

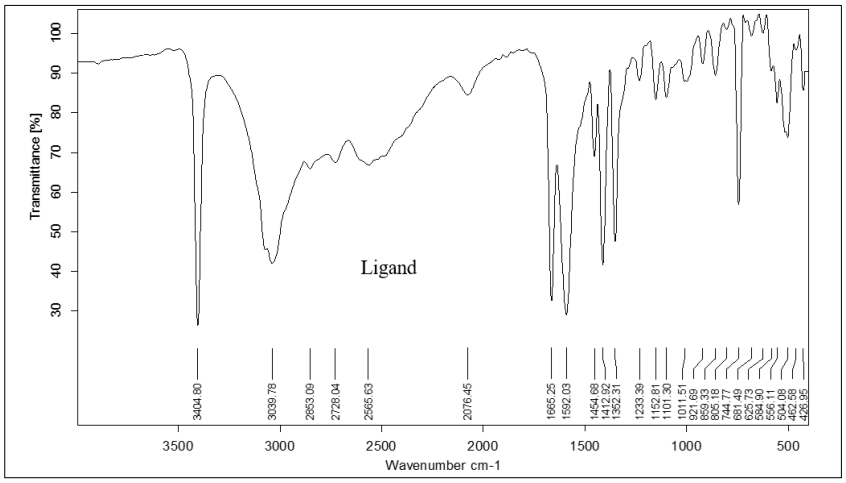
Since metal salts do not give spectra, but when metals conjugated with ligands, the complex gives IR spectra, the (IR) spectra technique is one of the most effective methods for studying the characterization of complexation between the ligand and the metal salts [9]. The structure of the prepared complexes was defined using infrared spectra, with the metal complexes' IR spectra being assigned by comparing their vibration frequencies to those of the ligand: The IR spectrum of Tryptophan and its complexes was reported for comparative purposes and to aid in the spectra assignment of the complexes. The obtained data are presented in Table (2) below.

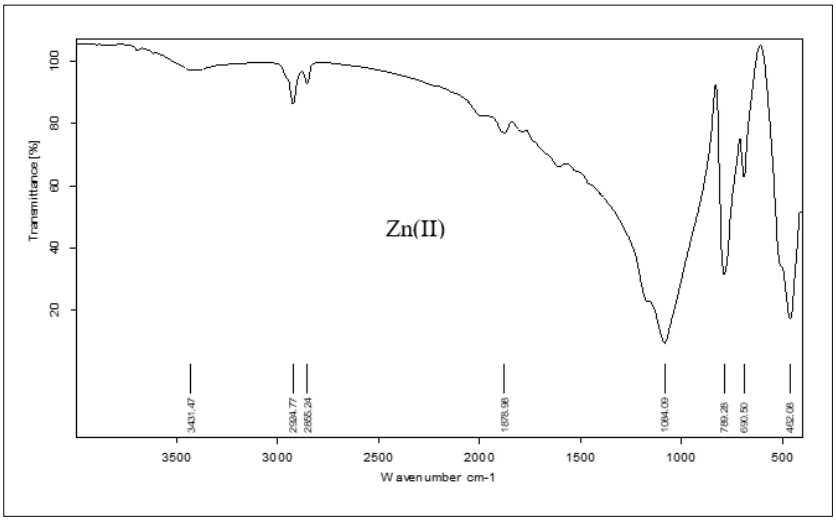
Table 2: The fundamental bands of the free Tryptophan and its complexes

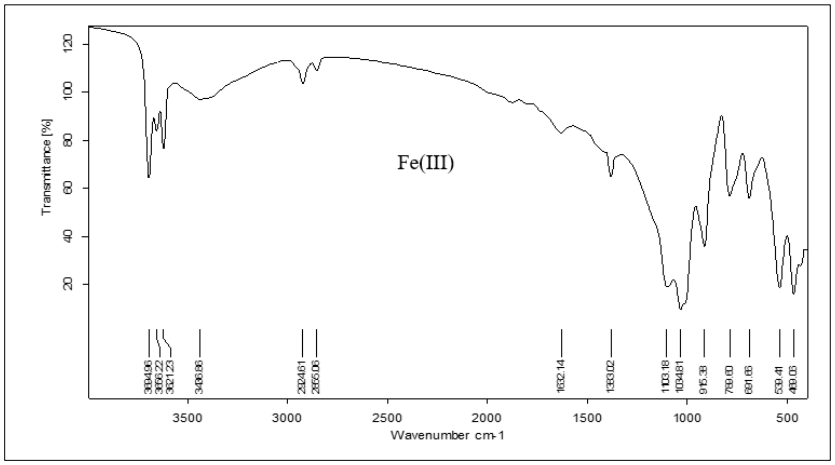
Complexes	Functional group											
	C-H Aromatic	C-H Aliphatic	C=N	C=O	C=C	CH_2	CH_3	C-O	C-N	N-H	M-O	M-N
L-Tryptpphan Ligand	3039	2853	1592	1665	1592	1454	1352	1233	1152	3404	-	-
Zn(II) complex	3125	2932	1620	-	1488	145o	1389	1277	1088	3404	692	490
Fe(III) complex	-	3040	1663	-	1453	1411	1351	1234	1150	3403	623	520
Cu(II) complex	3272	2907	1625	-	1456	1384	1350	1226	1151	3389	695	501

The main peaks of the IR spectra are shown in Figure (1), as well as the most significant absorption bands. In the ligand's spectrum (Tryptophan), the band of Ligand (Tryptophan) 3039 cm^{-1}are assigned to C-H aromatic, the first band of the Tryptophan shifted to higher frequency in Zn complex and Cu complex. Whereas, the same spectra display a band at 2853 cm^{-1}of Tryptophan are assigned to C-H aliphatic shifted to higher frequency in all complexes. Also the absorption band at at 1592 cm^{-1} of Tryptophan assigned to C=N, the band are shifted to higher frequency in Zn(II), Fe(III) and Cu(II) complexes compared to its position in the original ligand (1592 cm-1) indicating its involvement in coordination with the metal ions [12]. Whereas, the absorption band at (1665 cm^{-1}) was attributed to the carbonyl stretching vibration in the ligand were disappeared in the spectra

of all complexes suggests its participation as imines group in complexation [13]. The band C=C of Ligand appear in 1592 cm^{-1} shift to lower frequency in Zn(II), Fe(III) and Cu(II) complexes. The band CH_2 located at 1454cm^{-1} all complexes shifted to lower frequency. Also the absorption band CH_3 appear at 1352 cm^{-1} shifted to higher frequency as in the case of Zn complex but for the other complexes shifted to lower frequency. Whereas, the absorption band at 1233 cm^{-1} due to υ C-O vibration of the ligand is shifted to higher frequency except in case Cu (II) complex are shifted to lower frequency indicating its involvement in coordination with the metal ions through the oxygen atoms [14, 15]. The υ N-H band located at 3404 cm^{-1} are shifted to lower frequency in case Cu(II) complex, but there is no change in υ N-H group in other complexes this mean that this group is not entered in chelation. New bands observed at 692-695 cm^{-1} and 490- 501 cm^{-1} which are not seen in the spectrum of the free ligand can be attributed to υ (M-O) and υ (M-N) vibrations, respectively [16].







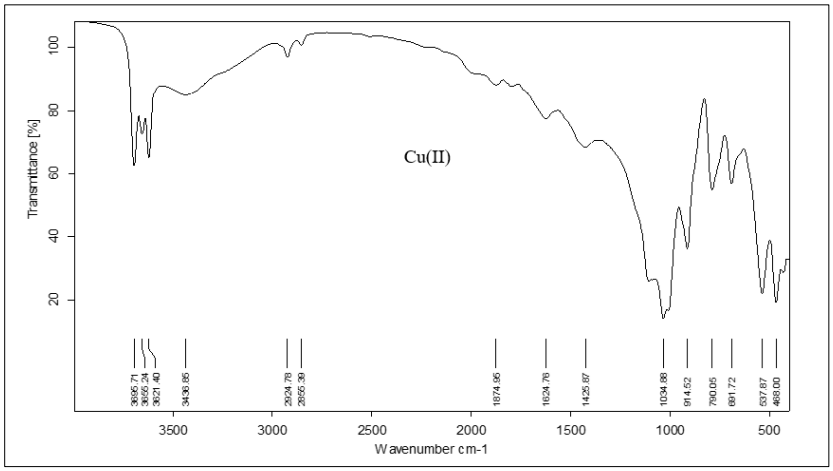


Fig 1: IR Spectra for Tryptophan and its complexes

Thermogravimetric Analysis (TGA)

The weight losses were calculated from ambient temperature up to 1000 ºC using a heating rate of 10 ºC/min [7], and the Thermogravimetric analysis of the complexes was performed to assist in predicting the molecular structures. We were able to determine the temperature at which the characterized compound has a constant weight and starts to decompose, as well as how far the decomposition reaction can proceed, using Thermogravimetric analysis curves [17]. The observed and stoichiometric weight decreases of the material allow for the estimation of an intermediate product produced during decomposition, as well as the temperature range at which this intermediate has constant weight [18]. The Thermogravimetric analysis data for some tryptophan complexes are given in Table (3).

Some examples of TGA curves of the prepared complexes were presented in Figures (2 - 4). The weight loss of Tr- Zn, Tr- Fe and Tr- Cu complexes corresponding to loss of water molecules at the temperature range of (99.6 to 263.9 ˚C). And the loss of CO_2 molecules were occurs at the temperature range (396.9 to 438.9) [19]. While the residual of metals oxides (MO_2) of (694.8 – 698.3 ˚C) rang was appeared.

Table 3: The thermogravimetric analysis data for tryptophan complexes.

Complexes	Decomposition		
	H_2O Temp. ^0C	CO_2 Temp. ^0C	MO_2 Temp. ^0C
Zn(II) complex	RT-263.9	426.7	697.3
Fe(III) complex	RT-188.2	396.9	694.8
Cu(II) complex	RT- 99.6	438.9	698.3

Based on the above findings. For the complexes under investigation, the following thermal decomposition scheme may be proposed as following:

$[ML.nH_2O].nH2O \rightarrow [ML.nH_2O]$

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

$[ML] \rightarrow$ intermediate (unstable)

Intermediate $\rightarrow$ Metal oxide MO_2

Intermediate (decomposition of organic ligand).

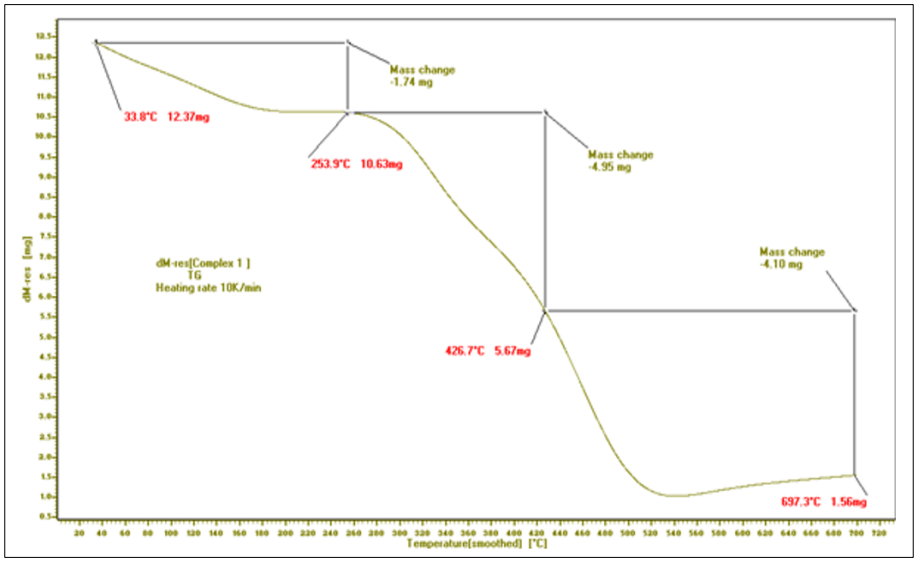


Fig 2: The TGA curve of Zn (II) complex

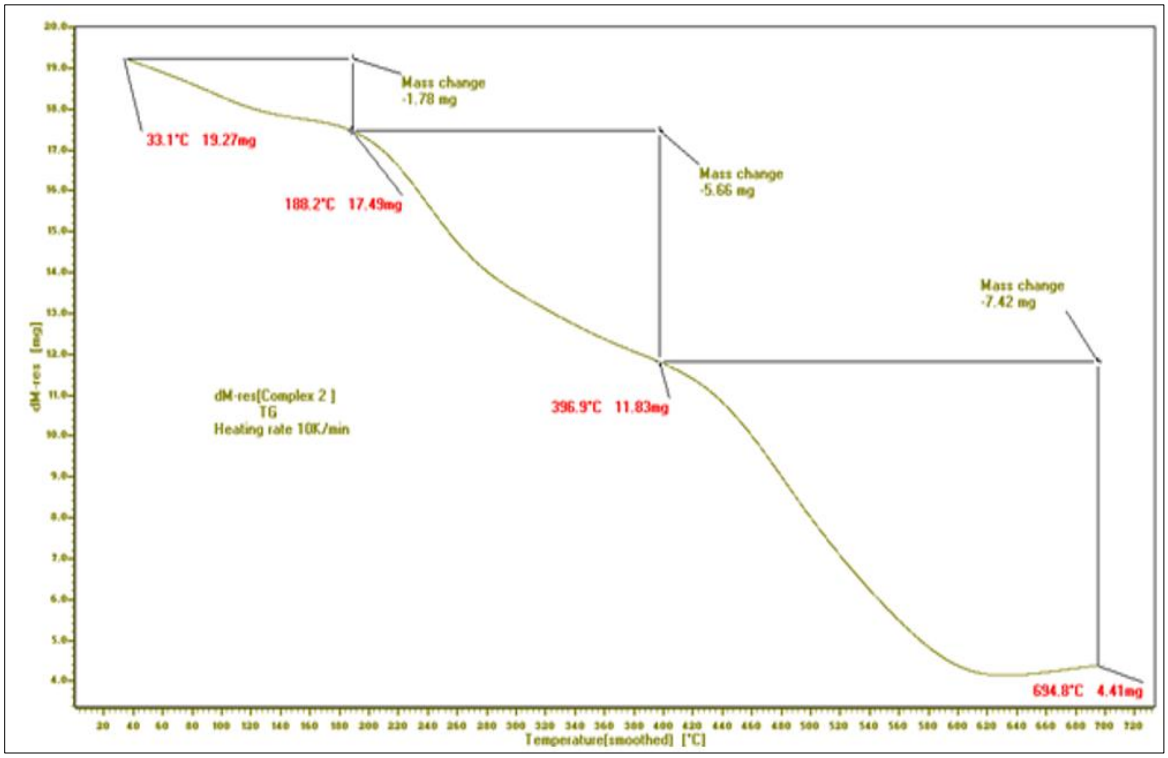


Fig 3: The TGA curve of Fe complex

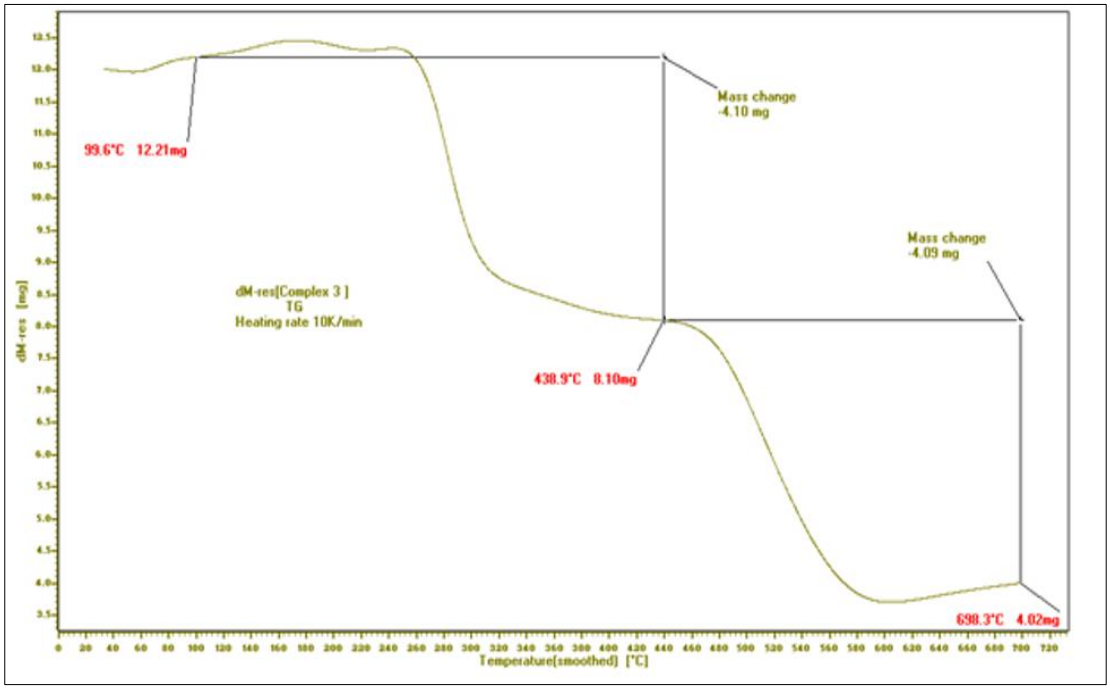


Fig 4: The TGA curve of Cu complex

Biological activity test

Effect of the three complexes on hatching of egg masses and mortality of the J_2s of Root knot nematodes (RKN). Result showed that eggs hatched after 3 days of incubation reached 237 J_2s in control and (107, 102 and 79) J2s at three concentrated of Zn(Il) complex and (12, 27 and 6) J_2s at three concentration of Cu(ll) complex when compared with the Fe(Ill) complex all concentrated were not effected on the egg hatching. However two Complexes (1, 3) and control were showed that relatively low percentages of died J_2s at all concentration, accept on complex 3 at higher concentration (0.09 mg) all J_2s died, compared with Fe(Ill) complex, the mortality % of J_2s were higher in all complexes, Table (4).

Table 4: The biological activity of the prepared complexes.

Treatment	complexes									
	Zn(Il) complex			Fe(Ill) complex			Cu(ll) complex			control
	0.01mg	0.05mg	0.09mg	0.01mg	0.05mg	0.09mg	0.01mg	0.05mg	0.09mg	Tap water
Egg hatching	107	102	79	+	+	+	12	27	6	189
Mortality %	-	-	2	100	100	100	29	23	100	-

+: Not egg hatching.
: Mortality of J_2s (%).

Reference

1. Eisenback JD, Triantaphyllou HH. Root knot nematodes: Meloidogyne species and races. In: manual of Agricultural Nematology, W. R. Nickle. (Ed). Marcel Dekker, New York,1991, 281-286.
2. Abu-Gharbieh, W. I., Karajeh, M. R. and Mosoud, S. H. Current Distribution of the Root Knot Nematodes (Meloidogyne species and races) in Jordan. Jordan Journal of AgriculturalSciences,2005:1:1.
3. Good game DML, Goodgame M, Hayward PJ, Rayner-Canham JW, Inorg. Chem,1988:7:2447.
4. Jin G-P, Lin X-Q. Electrochem. Commun,2004:6:454.
5. Ya Y, Luo D, Zhan Li, G C, Bull. Korean Chem. Soc,2008:29:928.
6. Hasan HMA, Abdulsayid FA, Bouagila RA. Journal of Applied Chemistry,2020:13(5):47-5.
7. Abdlseed FA, El-ajaily MM. International Journal of Research in Pharmaceutical and Biomedical Sciences, 2012, 3(3).
8. Bader YA, Zagazig L, Agric Red,2019:46:(6B).
9. Abdulsayid FA, Hasan HMA, Bouagila RA. International Research Journal of Pure & Applied Chemistry,2020:21(17):1-9.
10. Abdulsayid FA, Hasan HMA, Shuoaib AM, Bader YA. International Journal of Innovative Science, Engineering & Technology,2021:8:3.
11. Guerra C, Bickelhaupt F, Saha S, Wang F. phys. Chem. A,2006.
12. Morad FM, El-ajaily MM, Maihub AA, Egypt J. Anal. Chem,2006:15:98-103.
13. El-ajaily MM, Bomoraiwaha HF, Maihub AA, Egypt J. Anal. Chem,2007:16:36-46.
14. Tarafder MTH, Tan ML, Ali AM. United Nations Educational Scientific and Cultural Organization and International Atomic Energy Agency,2003,IC/112.
15. Doubell PC, Oliver DW, Arzneimittel Forschung,1992:42:(1):65.
16. Raman N, Raja YP, Kulandaisary A. Indian Academy of Science,2001:113:183.
17. Ahuja IS, Rastogi P, Inorg. Nucl. Chem. Lett,1999:5:255.
18. Boghaei MD, Sabounchi SJ, Rayati S. synth. React. Inorg. Met. Org. Chem,2000:30:8.
19. Edmonds BJ, Lever ABJ, Inorg Chem,1995:4:1608.