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Physical Studies, IR Characterization and Antimicrobial Studies of Complexes Prepared by Reactions between Lysine and Metal Ions of Co(II), Cr(III) and Cd(II)

[1.]Hamad.M.Adress.Hasan
Chemistry Department, Faculty of Science, Omar Almukhtar University, Libya
[2.]Hamdi.A.Khatab.Ali
Chemistry Department, Faculty of Education/ Almarj, Benghazi University, Libya
[3.]Mohammad.A.Musa
Chemistry Department, Faculty of Science, Omar Almukhtar University, Libya

Abstract
The coordination complexes of Co(II), Cr(III) and Cd(II) with Lysine were synthesized andcharacterized. The compounds were characterized using melting point, conductivity and infrared spectra.Antimicrobial study of thecomplexes was carried out, the tested microbes included Bacillus and Escherichia coli bacteria and Aspergillus niger and T2,32 fungi. The results of the melting point of the studied complexes showed different values between the free ligand and complexes.The results of conductivity were ranged between (2.4 -5.1), supports the presence of non – electrolyte nature for these complexes.The antimicrobial study showed the complexes possess activity against themicro-organisms.

Key words: *Complex ,Lysine, melting point, conductivity, IR,antimicrobial.*

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I. Introduction

A coordination complex consists of a central atom or ion,which is usually metallic and is called the coordination centre,and a surrounding array of bound molecules or ions that are in turn known as ligands or complexing agents. Many metalcontaining compounds, especially those of transition metals,are coordination complexes. A coordination complex whose centre is a metal atom is called a metal complex [1].The study of transition metal complexes containing biologically important ligands is made easier because certain metal ions are active in many biological processes [2]. The fact that transition metals are essential metallic elements and exhibit great biological activity when associatedwith certain metal-protein complexes, participating in oxygen transport, electronic transfer reactions or the storage of ionshas created attention in the study of systems containing these metals.The chemistry of transition metal complexes is well known. However, the evaluation of their antimicrobial activities has continued to attract more and more attention. This is because bacteria can cause foodborne disease[3] and also affect our lives; therefore, there has been constant effort to derive new antimicrobial agents [4][5].Coordination complexes of transition metals have been widely studied for their antimicrobial activities[5][6].Lysine (abbreviated as Lys or K), is an α-amino acid used for protein biosynthesis (proteinogenesis).There are many different kinds of amino acids, but only twenty are used universally by all forms of life for protein synthesis (i.e., proteogenic amino acids). The process of translation is how proteins are synthesized and lysine is added at the codons AAA and AAG. Lysine is an essential amino acid to all animals, including humans, and therefore must be obtained through dietary intake[7][8]. Bacteria, archea, fungi, some Protista (euglenids), and plants, on the other hand, are able to synthesis lysine. The organisms that are able to synthesis lysine can be thought of as the primary producers,on which all animals are dependent for their nutritional lysine requirement. Two different pathways have been identified in nature for the synthesis of lysine. The diaminopimelate (DAP) pathway belongs to the aspartate derived biosynthetic family, which is also involved in the synthesis of threonine, methionine and isoleucine[9][10] Whereas the α-aminoadipate (AAA) pathway is part of the glutamate biosynthetic family[11][12].Lysine is one of the nine essential amino acids in humans.[13] The human nutritional requirements variesfrom ~60 $mg.kg^{-1}$ in infancy to ~30 $mg.kg^{-1}$ in adults.[8] This requirement is commonly met in a western societywith the intake of lysine from meat and vegetable sources well in excess of the recommended requirement.[8] In vegetarian diets, the intake of lysine is less due to the limiting quantity of lysine in cereal crops compared to meat sources.[8]. The most common role for lysine is proteinogenesis. Lysine frequently plays an important role in protein structure. Since its side chain contains a

positively charged group on one end and a long hydrophobic carbon tail close to the backbone, lysine is considered somewhat amphipathic . For this reason, lysine can be found buried as well as more commonly in solvent channels and on the exterior of proteins, where it can interact with the aqueous environment.[14]. Lysine can also contribute to protein stability as its ε-amino group often participates in hydrogen bonding, salt bridges and covalent interactions to form a Schiff base[14][15][16][17].Lysine has also been implicated to play a key role in other biological processes including; structural proteinsof connective tissues, calcium homeostasis, and fatty acid metabolism[18][19][20]. Lysine has been shown to beinvolved in the crosslinking between the three helical polypeptides in collagen, resulting in its stability andtensile strength[18][21]. This mechanism is akin to the role of lysine in bacterial cell walls, in which lysine (and*meso*-diaminopimelate) are critical to the formation of crosslinks, and therefore, stability of the cell wall.[22]This concept has previously been explored as a means to circumvent the unwanted release of potentially pathogenic genetically modified bacteria. It was proposed that an auxotrophic strain of *Escherichia coli* (X1776)could be used for all genetic modification practices, as the strain is unable to survive without the supplementationof DAP, and thus, cannot live outside of a laboratory environment[23].

II. Materials and Methods

All chemicals were obtained from commercial sources and were used without further purifications ($CdCl_2.4H_2O$, $CrCl_3.3H_2O$ and$CoCl_2H_2O$),P_2O_5, and distilled water. Lysine was obtained from BDH.The conductivity values of the prepared complexes were measured by using (conducto meter , type HANA).Melting point was measured by using machines type(Melting point Apparatus SMP3). 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}

2.1.Synthesis of metal –L-lysine - complexes:

0.8 mole of metal chloride in 50 ml ammonia was added with stirring to 0.6 mole of lysine 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.

2.2. Biological test:

2.2.1. Bacterial cultures:

Plate cultures of nutrient agar (OXID) medium were used for culture of bacteria . the medium was prepared by dissolving of powder in 1liter of sterile distilled water . Then the medium was sterilized by autoclaving at 121 C^0 for 15 minutes. The bacteria were cultured and incubated at 37 C^0 for 24h.

2.2.2. Antibacterial assay:

The antibacterial tests were assayed according to the diffusion method. The strains of bacteria used were Gram-positive and Gram-negatve bacteria (E.coli , Bacillus). All strains were isolated from patients in medicine academe .The identity of all the strains was confirmed. A bacterial suspension was prepared and added to the sterilized medium before solidification under aseptic condition.Different weights of amino acid complexes, Cr(lIl),Co(ll),Cd(II) (0.1g from complex in 1litter) were placed on the surface of the culture and incubated at 37C^0 for 24h. After incubation the average of inhibition zones recorded (μm).

2.2.3.Anti fungi test:

200 grams of potatoes were cut into cubes and added to 1000 ml of distilled water for half an hour, then filtered and placed in a graduated tester and added 20 g glucose in addition to 23 g agar and the inserted tester is filled with distilled water to 1000 ml.Then placed in a tightly sealed flask and put on flame for a quarter of an hour to half an hour, then sterilized, after sterilization is poured into dishes. The antifungi tests were assayed according to the diffusion method and used fungal species yeast (Aspergillus niger , T2,32fungi). All strains were isolated from patients in medicine academe .The identity of all the strains was confirmed. A fungi suspension was prepared and added to the sterilized medium before solidification under aseptic condition. Different concentrations of Schiff base complexes were placed on thesurface of the culture and incubated at 28C^0 form 2 to 3days . After incubation the average of inhibition zones recorded (μm) .

III. Results and Disscusion

3.1. General Properties

The physical properties of the prepared complexes as (colors ,conductivity and melting point were given in Tables (1) . The color of ligand was change from white color of the free ligand to several different colors according to the type metal , this change mainly due to the effect the linkage between the ligand and for to the different of electrons in 3d orbital's ,where during the attracting between the ligand and the metal the electrons which are in d orbital and portion them for groups the high and less in energy ,the magnetic frequency beam is proportion with the different in energy between the two states energy in atom. Some electrons rise into energy high level. The results of the melting point of the studied complexes showed

different values between the free ligand and complexes, this different mainly attributed to the bounded between the metals and the ligand. The results of conductivity were ranged between (2.4 -5.1), supports the presence of non – electrolyte nature for these complexes, also these values indicated that no anions existed outside the coordination sphere.

Parameter / Complex	Color	E.C(**μ**S)	**M.P (^{0}C)**
Ly – Cr	Green	4.8	239
Ly – Co	Pink	2.4	200
Ly –Cd	White	5.1	221

Table (1): The colors, conductivity and melting point of Lysine complexes.

3.2. Infrared spectra studies:

Selected Infrared absorptions of the ligand and their complexes are shown in table (2). The bands of lysine are located at 3490.91 cm^{-1} ,3096.53 cm^{-1} and 1531 cm^{-1} are assigned to N-H and δ N-H and C = O respectively [16]as shown in figures(1-4).The first band of the free ligand is shifted to higher frequency in case of the most complexes (Cd, Cr, and Co). On the other hand, The δ N-H ligand band is subjected to changes in position in the Cd and Cr 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. 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. The band at 1409 cm^{-1} is slightly shifted in case of cadmium , chromium and cobalt complexes and shifted to lower frequency .Such finding suggests that the carboxyl group takes part in the cobalt complex through deprotonation.[24]. 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[25]. 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 - the inter 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[19] Also, the metal-nitrogen stretching frequencies can occur over a wide range, viz. from 600 to below. 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 Co complex. Based on the I.R data of the Fundamental groups (N–H, NH_2 and COOH) and the data obtained from the electronic measurements gathered with the elemental analysis.

Complex	**OH(H_2O)**	**NH_2**	**C = O**	**M –O**	**M - N**
Cd-Ly	3379	3041	1660	604	486
Cr-Ly	-	3039	1597	810	475
Co-Ly	-	3154	1593	840	490

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

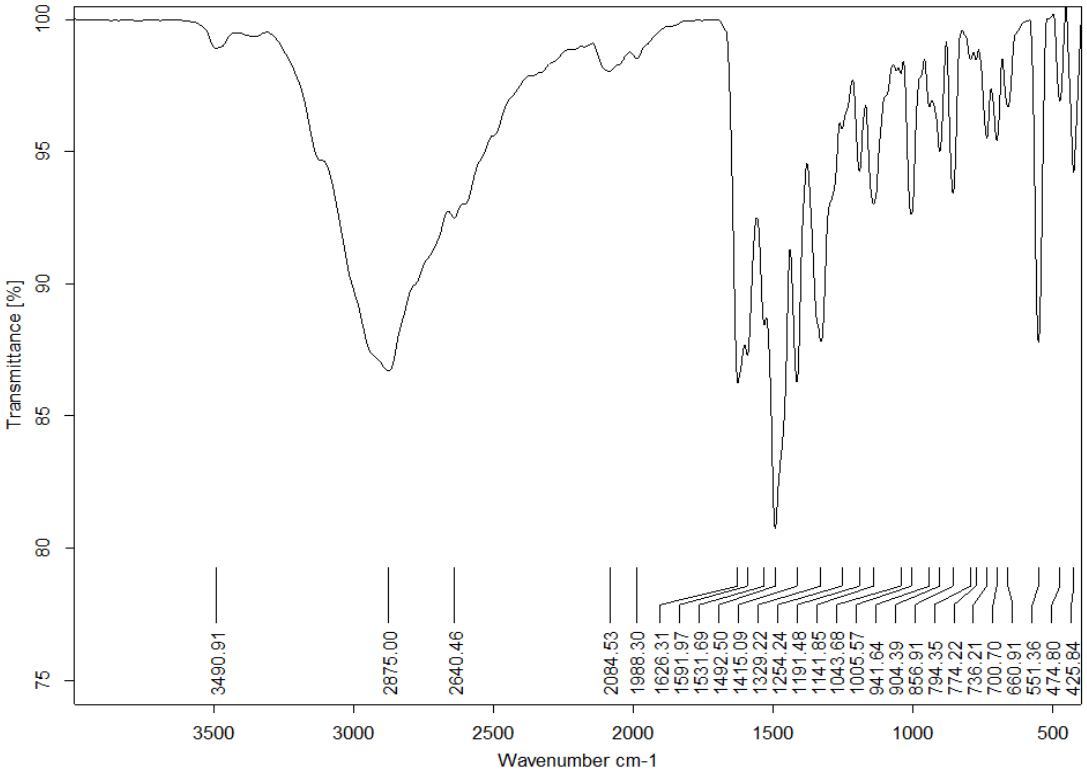


Figure (1) : The infrared spectra for the ligand (Lysine).

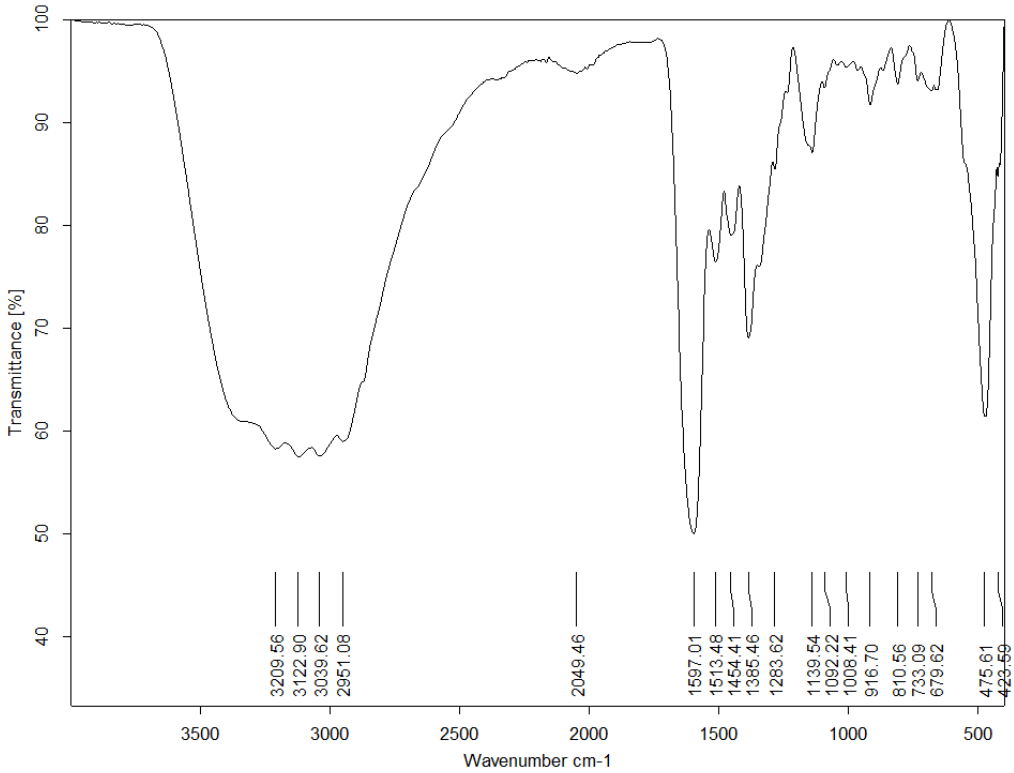


Figure (2): The infrared spectra for the ligand (Lysine) with Cr.

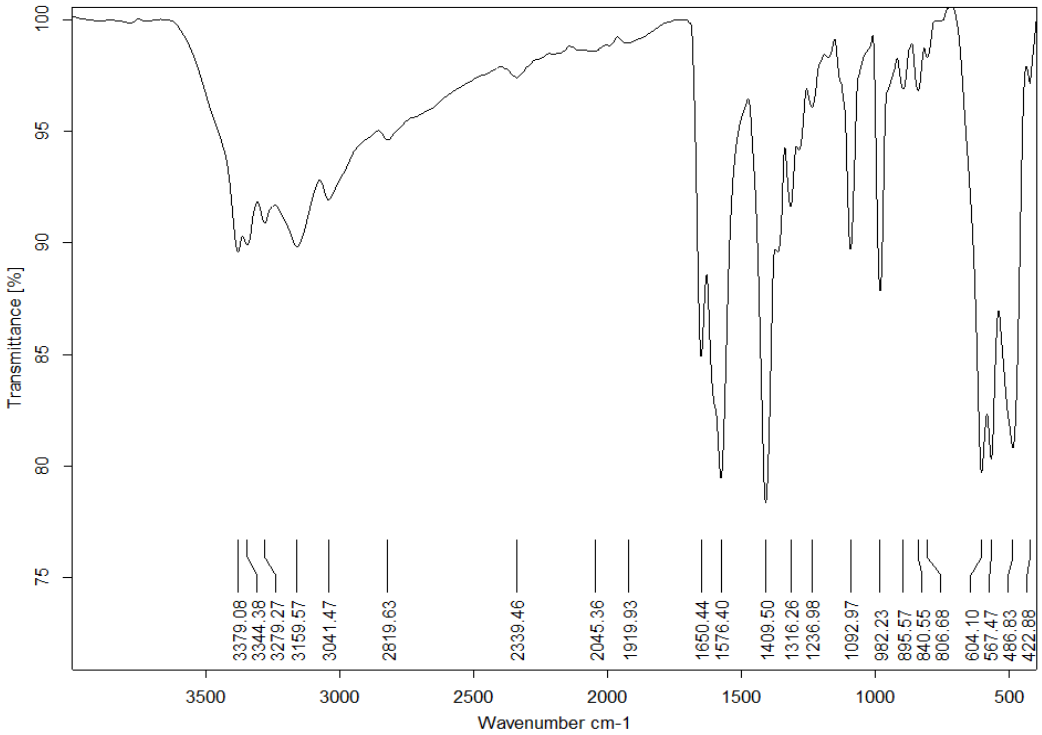


Figure (3): The infrared spectra for the ligand (Lysine) with Cd.

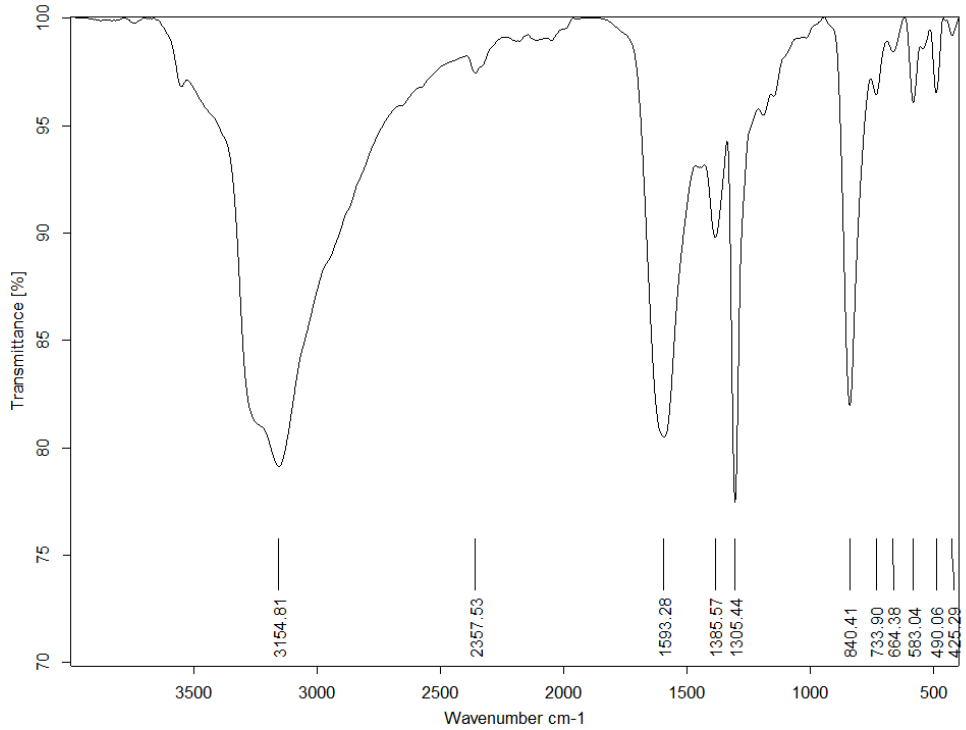


Figure (4): The infrared spectra for the ligand (Lysine) with Co.

3.3. Biological studies:

3.3.1.Antibacterial activities of Lysine complexes:

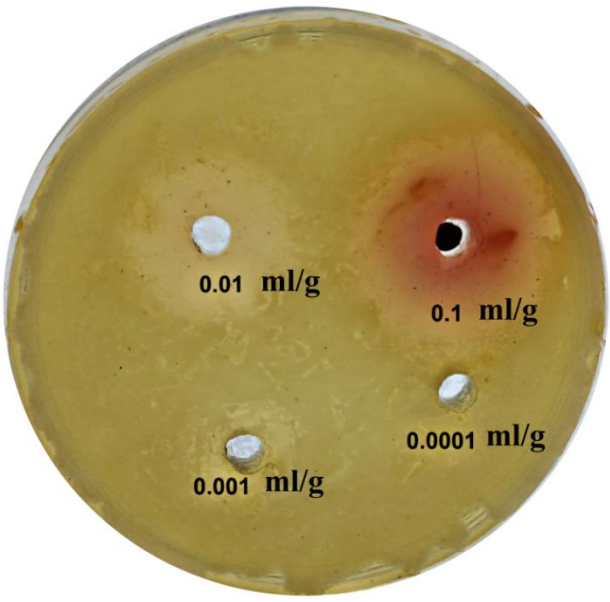
Table (3 and 4) and Figures(5 - 9) showed the inhibition zone of bacterial growth of Lysine complexes with Co(ll), Cd(ll) and Cr(ll), and Cd(ll) complex has a highest activity against E.coli , Bacillus. The results show the reduction of inhibition zone with the reduction of the compounds weight placed on the bacterial culture. The effect of Lysine complexes on bacteria was recorded only against Bacillus ,Escherichia coli.

The effect of lysine complexes on E.coli bacteria				
concentration	**10.**	**0.01**	**0.001**	**0.0001**
Cr- Ly	0.7cm	0.4cm	_	_
Cd-ly	2cm	1.5cm	1cm	.5cm0
Co-Ly	1.1cm	0.7cm	0.3cm	_

Table (3):The effect of lysine complexes on E.coli bacteria

The effect of lysine complexes on Bacillus bacteria				
concentration	**10.**	**0.01**	**0.001**	**0.0001**
Cr- Ly	0.4cm	0.3cm	_	_
Cd-ly	1.6cm	1.3cm	1.1cm	0.5cm
Co-Ly	1.8cm	1.4cm	1cm	_

Table (4): The effect of lysine complexes on Bacillus bacteria



Figure(5) Effect of Co lysine complexes on bacillus

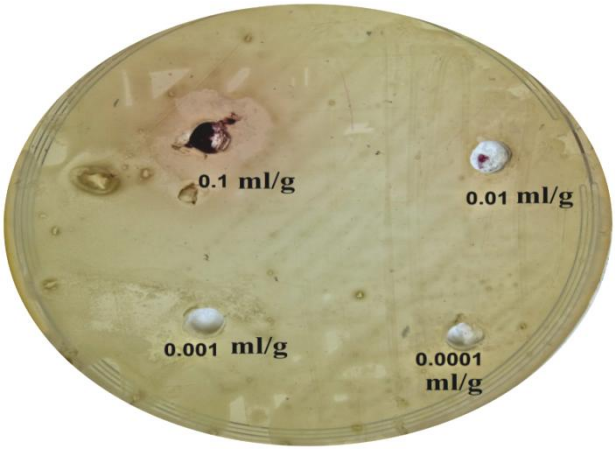


Figure (6):effect Co lysine complex on Escherichia coli.

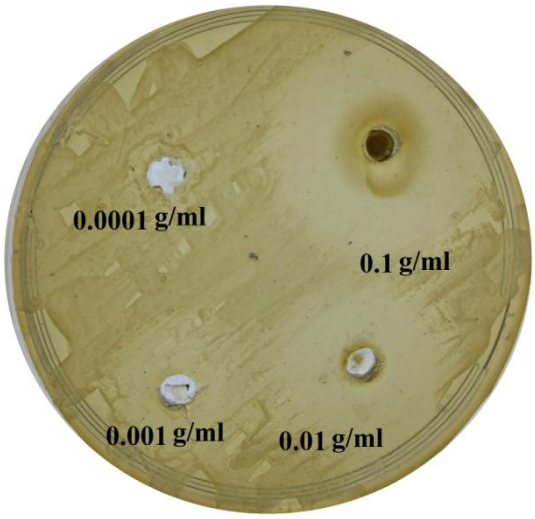


Figure (7):effect of Cd Lysine complex on Escherichia coli.

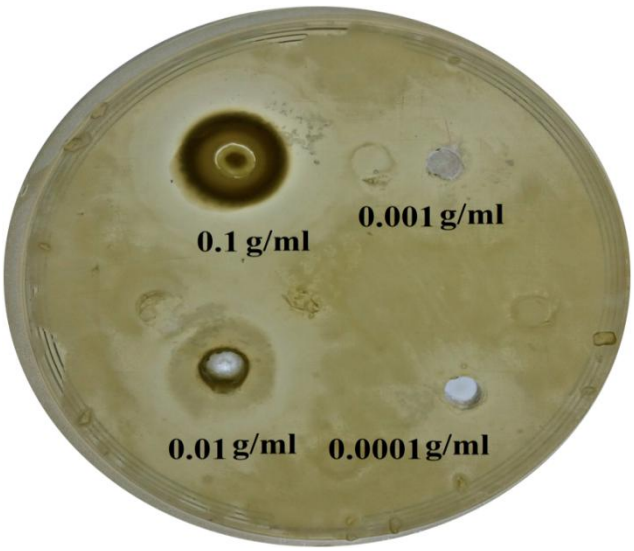


Figure (8):effect of Cd Lysine complex on Bacillus.

Figure (9):effect of Cr Lysine complex on Escherichia coli.

3.3.2.Antifungi activities of the Lysine complexes:

Table (5,6) and Figures(10-15)show the inhibition zone of fungi growth of Lysine with Co(ll), Cd(ll),Cr(lIl) complexes and Cd(ll) complex has a highest activity against Aspergillus niger , T2,32fungi. The results show the reduction of inhibition zone with the reduction of the compounds weight placed on the bacterial culture.The effect of Lysine complexes on fungi was recorded only against Aspergillus niger , T2,32.

The effect of lysine complexeson Aspergillus niger fungi				
concentration	**0.1**	**0.01**	**0.001**	**0.0001**
Cr- Ly	1.4cm	0.3cm	–	–
Cd-ly	2cm	1.6cm	1cm	0.5cm
Co-Ly	2cm	1.5cm	–	–

Table (5): The effect of lysine on Aspergillus niger fungi

The effect of lysine complexes on T2,32 fungi				
concentration	**0.1**	**0.01**	**0.001**	**0.0001**
Cr- Ly	1cm	–	–	–
Cd-ly	3cm	2cm	1cm	–
Co-Ly	1.5cm	0.5cm	0.2cm	–

Table (6): The effect of lysine on T2,32 fungi

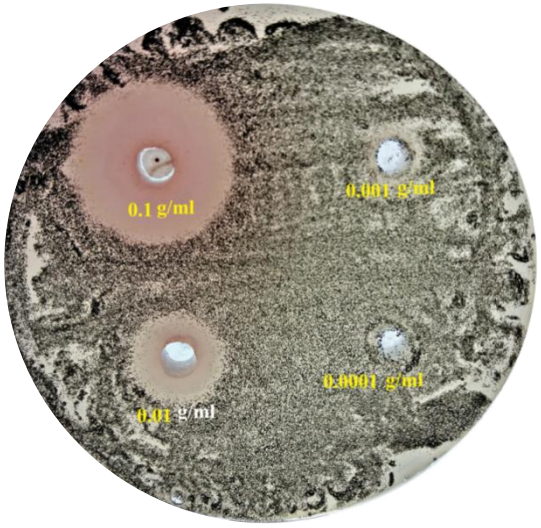


Figure (10):effect of Co Lysine complex on A.niger.

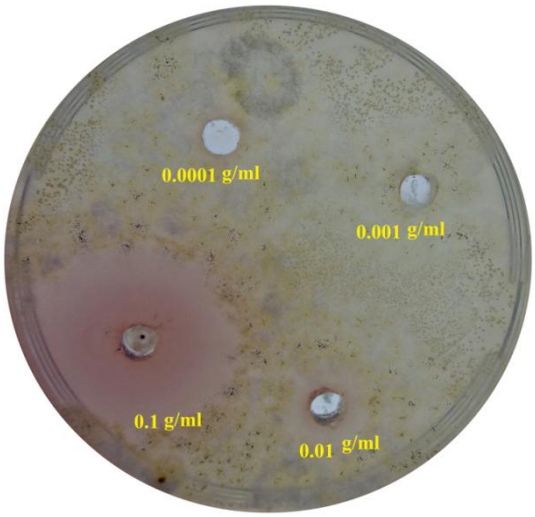


Figure :(11):effect of Co Lysine complex on T2.32.

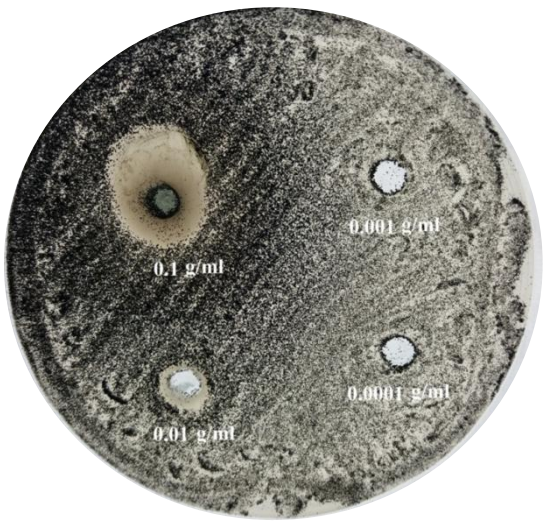


Figure (12):effect of Cr Lysine complex on A.niger.

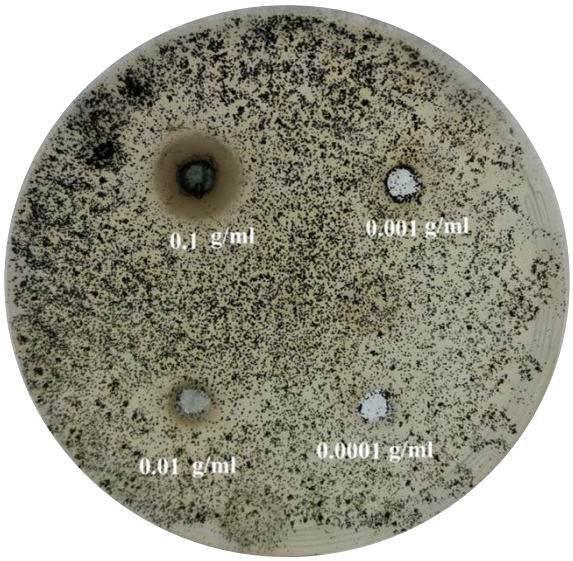


Figure (13): effect of Cr Lysine complex on T2.32.

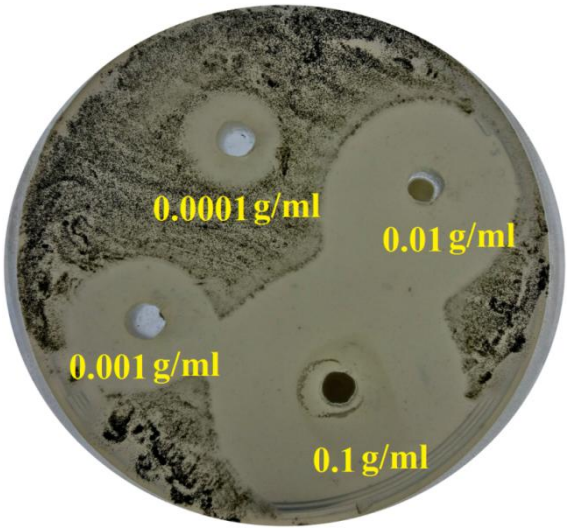


Figure (14):effect of Cd Lysine complex on A.niger.

Figure (15):effect of Cd Lysine complex on T2.32.

IV. Conclusion

In this work lysine complexes of Cd(II),Cr(II) and Cr(III) were synthesized by direct reactionand using some properties and spectral studies to identification the complexes, the data showed that most of the metals which selected gave complexes with the ligands.The effect of Lysine complexes on bacteria was recorded against Bacillus ,Escherichia coliand Cd(ll) complex has a highest activity against E.coli and Bacillusbacteria.The effect of Lysine complexes on fungi was recorded against Aspergillus niger and T2,32 fungi. and Cd(ll) complex has a highest activity againstAspergillus niger , T2,32 fungi.

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